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EPA/NARSTO PM MEASUREMENT RESEARCH WORKSHOP

"Breakout Group; PM Measurement Methods"

July 22, 1998

MS. HERING: I'd like to welcome everybody to our measurements breakout session. A couple of things, first of all, I mean the reason for these workshops, at this point is not to get, not for us to stand up here and give you information. More it's to get ideas and inputs from those of you who've come so far to come to the meeting. So, that's the context of all of this. I do need to mention that, for various EPA reasons, we do have a Court Reporter here, who's going to be recording comments and he's going to want to know who you are. So, when you say something...so, I'll start off. I am, so when you make your comments, once we get the door shut, then hopefully other people will still come. If you would say who you are and I should start off by introducing myself.

I'm Susanne Hering from Berkeley, California and our two co session leaders, Kurt Anlauf from Canada and Russ Wiener from EPA. I sort of joked, the reason I got this job, I tried very diligently to be quiet

when they asked for volunteers for discussion leaders, but I happened to go out of town and so I got the job, so that's what happened here. Just to remind you, this was a slide from...I'm going to stand over here...from the talk this morning. I think everybody recognizes that doing detailed measurements, ambient particles... There's a seat here, just please come on in. Doing ambient measurements, measurements of ambient particles is a challenge because there's so many parameters that could possibly be measured and there are, in the long term especially, only so many dollars that can go along, around to do the measurements. As the most expensive part of looking at new methods, often times is not just coming up with the ideas, but also validating and evaluating how good those methods are and what are the strengths of those methods and what are the weaknesses of those methods. So, when they're, when we have the opportunity at these super sites, the idea is proposed and I think everybody agrees, that we would like to use the opportunity of concurrent measurements to build measurement methods for the future. I just broke this down into identifying needs, identifying promising approaches and then looking at specific things that we would like to compare in the field.

With regard to identifying needs, I've just made this list out of the document that you were given,

that is the 10 culprits from the health perspective, 10 possible characteristics of airborne particles that might be a reason for observed statistical relationships with health effects. The exposure assessment chapter that was put forth by Paul Lioy added to this list, saying that in addition to the parameters on the health list we need to know temperature and relative humidity, the meteorological parameters. We need to know the gases, I guess that's under co-pollutants as well, and he suggested measurements for the chemical sites. These are the so called PAM sites where they are hydrocarbon, speciated hydrocarbon measurements, complete aerosol chemistry and temporal profiles. A chapter on receptor measurements listed also multi phased, semi volatiles speciates that partition back and forth between the gas and the particle phase and measuring those in both phases. They mention doing size result chemistry, as in impact of measurements, to find out whether the size distribution is specific to chemical components. Measuring the physical size distribution, measuring light scattering, light absorption, looking at levels of clouds and fog. Upper level mass and getting high time resolution for the purposes of model source resolution.

This is sort of a list here and what I would like to do, since this is a discussion, I would like to get comments really from the audience. First of all, with

regard to the questions of what measurements, what measurement methods are, things that need to be measured that we don't have currently accepted methods for, that would be good to assess the performance of in the field.

MR. SOLOMAN: Since you wanted me to talk, I'll get things started. Paul Soloman, EPA. One of the conclusions from this list, particularly in the role of source receptor, would be free phrase. Because if we're going to do source receptor in terms of emissions phase model, chemical model that would be very useful to us, in helping to evaluate, further evaluate the emissions phase models.

MS. HERING: We probably should see that. Okay. Well, since we started on source receptor, any comment, any additional?

MR. LEWIS: Chuck Lewis from EPA. Need to consider radio carbon measurements, biogenic component.

MS. HERING: Okay. Now what I'm...now our job here, all right, is to...okay. This is just to give an idea of a list of parameters and then we can talk about, the idea then was to look at measurement methods. It's not our job here to design the measurements.

MS. CHOW: Spatial, part of source receptor.

SPEAKER: I have a question. Why do you have time resolution only under source receptor? I mean there's...

MS. HERING: You could put it up here as well, right? I would agree with that.

SPEAKER: If you don't have the right time resolution for your health effects, you're going to miss it.

MS. HERING: So, should we, maybe a vertical receptor.

SPEAKER: Just put it up top, because it's all three. Health effects.

MS. HERING: So, maybe I'll turn, having to orient ourselves with the list here, since this is measurement methods, maybe I'll turn this over to look at the actual measurements and identifying methods that, or approaches that people here in the room think are important to have that at, the intensive measurement sites, be they the more intensive of the speciation sites or be it at the super sites, as they're called, for method validation purposes.

MR. ALLEN: Dave Allen from the University of Texas. Susanne, I wonder if we could take a step back and one of the things that really strikes me about a room like this is, we all probably have really innovative ideas about novel measurements that could be made. I guess I pose the question, are

these super sites going to have a controlled slate of measurements that will be made consistently and then the sites will essentially do that and that alone, or can they also be research platforms, where investigators, with a bright idea, who might have a new measurement, to which they want to compare to all the other existing measurements, could get space at a super site to make such measurements?

SPEAKER: It's on sale today.

MR. ALLEN: I'd like to suggest that.

MS. HERING: So, it's our job to make recommendations.

MR. ALLEN: That these be regarded not only as data collection enterprises, but also as platforms for investigators to demonstrate new technologies.

SPEAKER: It's actually the objective of the super sites, is to put the new technology out there, test it...

MR. ALLEN: Well, the way...

SPEAKER: ...transfer and compare.

MR. ALLEN: But the way I read that was existing things that are in the labs now, that the research instruments, if we want to put it at the super sites, then it will eventually make their way into the speciation sites. What I'm proposing is something, a measurement that maybe none of us has an idea in the

room today, that can be made.

SPEAKER: Speaking from the health sector, one of the things we are constantly addressing, is using collected particles in which obviously some of these are in collection. I see all these endpoints being measured here. Is there any thought as to how do devise part of the collection with minimal alteration or loss of the particle, because that would have a very good, very significant impact in the health field.

MS. HERING: Are you referring to particles that can then be resuspended?

SPEAKER: Yes, that can be used in a toxicological study.

MS. HERING: That's a challenge.

SPEAKER: This would be in the new technology area, as being brought out in the process.

MS. HERING: So, you want to be able to, for health effects, health studies...

SPEAKER: How can particles be collected with minimal loss of constituents, such that we get an accurate representation of the toxicology?

MS. HERING: But you want to collect them and be able to resuspend them?

SPEAKER: Well, collect them even if they're on the filter.

MS. HERING: Okay.

SPEAKER: If you do not lose VOCs

or you do not lose ammonia.

MS. HERING: So, collection alone is good enough, if it's accurate?

SPEAKER: Yeah.

SPEAKER: Or either we know how much these constituents are actually lost.

MR. ALLEN: Steve Allen from the University of Texas. I'd like to add the idea that you just mentioned, as being able to resuspend archived particles later or collected particles later for health studies. That's the discussion I've had.

MS. HERING: It's more of a challenge, I might say, because I don't know with a particle. I'll put it down here.

MR. ALLEN: Lots of challenges here.

MR. WHITE: Kurt White, United States Department of Energy. I'm interested in sample storage for later analysis. I think that we're going to have a big problem here if we don't have a good sample storage capability that we know works. If we want to go back six months later and look at that sample, we need to know how to store it.

MS. HERING: Yes.

MR. WHITE: So that it means something when we come back.

MR. McGEE: John McGee, U.S. EPA. As regards all these things that we're talking about, can

we have methods available to say health effects researchers who would like to use sampler methods that are compatible with our, say establishment? It's not the research methods. So that when we want, so that we have an apples to apples, as best we can, comparison of the data, we take the data that's taken throughout the country.

MS. HERING: I think we, I'll put this, it backs up as to what is a sort of established method.

MR. McGEE: Or methods.

MS. HERING: Methods.

MR. McGEE: Very frequently we do our literature searches and see like three referenced ones currently in use.

MS. HERING: So, you see as...

MR. McGEE: I would like to see like a web site or for whatever the methods are going to be used in the field, or the methods currently used by monitoring, so that we can keep our methods compatible and not be using some out dated method that's our re-invention of the wheel.

MS. HERING: Also, I would guess that in conjunction with the first item here, that you would like to have this suite of possible reference methodologies at the super sites for comparison with advanced methods. I think the only particle reference method right now is the PM2.5 mass one and the PM10

mass one.

MR. McGEE: For example, how, if we would like to remove atmospheric ammonia, if we wanted to do aerosol acidity measurements, I just looked that one up and got three methods. I'm not sure which would be the best to use.

MS. HERING: There could be some debate on that actually.

MR. McGEE: Well, sure. But just some way that we can keep our methods the same, as the research from all over.

SPEAKER: I think some of that's being addressed even in the speciation sites, to try and come up with very comparable methods so that you can utilize the same technology and methods across these sites, so that certainly these 50 sites with the speciation network, so that there is a direct comparability of analyses that someone is not using a super sensitive method and they get 10 more hits than somebody that uses something else. So, that's part of what I'm talking about.

MR. HARPER: Martin Harper, SKE. At the end of the day, you really don't want to measure any of those 10 items up there. What you want to measure is a health effect and there are some studies being done now, where mechanisms of the health effects of these items are being studied. For example,

I'll suggest ultra fine particles and enzyme inhibition. I think it would be a really great service if some of those ideas could be tested at a sampling site. For example, you could take the enzyme that you think is being inhibited, you can immobilize it and expose that at the same time that you're taking the sample and see exactly whether that is a logically plausible mechanism.

MS. HERING: How would I list that? I don't know what I would call that.

MR. HARPER: Biological makeup, testing biological causal mechanisms.

SPEAKER: In a measurement context.

MS. HERING: In a measurement context. I don't know what we do, but we'll list it. I'll call it testing mechanism. How about this, biological mechanistic testing methods, since this is a methods discussion. Pete?

SPEAKER: I don't think you've explicitly mentioned particulate water.

MS. HERING: No. Where is that? Source receptor, yeah. Actually could be relative. It could possibly relate to health, just from the point of view of what happens to a particle when you bring it in, what happens to the particle when it's exposed.

SPEAKER: In organics, transitional metals...

MS. HERING: They've got sulfates and nitrates.

SPEAKER: So, transitional metals is something else.

MS. HERING: Transition metals.

SPEAKER: Transitional metals like Chromium 3, 6, all those things could cause...

MS. HERING: I think that's a reason for that.

SPEAKER: Acceptable measurement for example.

MS. HERING: Oh, you mean fro mass measurements?

SPEAKER: Yeah. In terms of collecting that.

SPEAKER: The Federal Register requires that you condition the samples in a balance room that's got 30 to 40 percent relative humidity and you make your mass measurement after it's been reconditioned in that same room at that relative humidity. So, I would think in answer to his question, is there any specified humidity, yeah, 30 and 40 percent.

MS. HERING: Yeah, for the mass measurement, yes.

MR. HIGUCHI: John Higuchi, South Coast Air Quality Management. I just walked into this

conference right now, so I apologize. One bullet you had up there was method consistency and it was mentioned about speciated data. There's a lot of data that we collected last year and it involved speciation. We don't want to be so tied as to lock out any other valid data that was collected in the past.

MS. HERING: Oh, yeah, I don't think that's the notion here, to...maybe the question is evaluating consistency among methods. That's what we're really looking at here.

SPEAKER: Data comparability also.

MR. ALLEN: Dave Allen, University of Texas. I think an area that needs a lot of attention is the development of standards. Particularly, I mean, I used to be able to buy a sample of urban particulate matter from the MBS. That's really the only reference standard we have an all of us now just develop our own reference standards in laboratories. We don't have any commonality of reference standards. I think that it's not an entirely straightforward matter to say, what is the reference material, particularly for the organics, which is my strongest interest.

MS. HERING: Well, I think...

MR. ALLEN: So, I think that an effort needs to go into developing a reference material that will be realistic. The concern is the reference standard as we develop some of these methods, particularly for

the organics.

MR. McMURRY: Pete McMurry, University of Minnesota. There's another thing, I don't know if it belongs here, but I think we need to put some thought into archiving data, databases, development of software, that makes data, archived data readily accessible to people who may want to come back in the future to look at it. We all know of studies that have been done and the data is out there, but it's not necessarily easily gotten.

MS. HERING: Format is a big question.

MR. McMURRY: Format and access and documentation.

MS. HERING: And it relates to your question with the south coast data. I mean many people would be interested in that, if there were some easy way to make it accessible, right?

MR. McMURRY: Can I comment on that? I mean NARSTO has a database management system that is being used widely now. That's gone a long ways probably in addressing that issue.

SPEAKER: One point that is not stressed really is validation, validation of metals. I fear that many methods are now in use, even as reference metals, semi reference metals which are not very good, especially filter methods for nitrate and

other semi volatile species. The validation of this kind of problem, and it's reasonable to do this problem, will be a huge effort, because it has never been rigorously done. In Europe, to some extent, but also not really.

MS. HERING: I think our idea, and I agree with you, our idea here was to get a list of parameters and things that needed to be addressed by methods, look at possible methods and also define how we can cross compare these in the field and what parameters need to be there to say whether or not, or to what extent such and such a comparison is valid. There was a question in the back and you never got a chance. No?

SPEAKER: I attended two activities seminars before this workshop, and this workshop also. When you look at the analytes coming up, but when you collect one and you collect another on top and you're going to keep that sample and all that, they're going to react. So, there should be some preparation for three different types of analytes and what happens to them. We can't neglect chemistry completely.

MS. HERING: So, you're referring to the storage issues, reactions here on the storage, actually during sampling?

SPEAKER: What I'm saying, some attention should be given to that important aspect of sampling.

MS. HERING: So, chemical reactivity or synergies involved.

SPEAKER: Artifacts.

MS. HERING: I think what you really mean is artifacts caused by chemical reactions in sampling and storage. Standards is only one step here.

SPEAKER: Someone was asking about measurement of water in the samples and how do you do it. There's, I don't know if it will work for these air particulates, but there are some NMR methods that one can use to get total water. There's some ASTM methods available to do water and solids, that are pretty good. I don't know how low we'll need to go here, but they do work on many solids. For example, the food industry has got to measure the water content of various grains, oats and corn and what have you and they do it by NMR methods. That will give you a pretty good handle.

MS. HERING: Water content NMR. Mind if I put question mark down there?

SPEAKER: Yeah, by all means, because I don't know if it will work on these samples.

MR. MERRIFIELD: I guess one point...

MS. HERING: Tom Merrifield.

MR. MERRIFIELD: Tom Merrifield with Met One. ...is the point of economics and what we

can afford to do here. We've got a wonderful list but I guess I look at it on the basis that these super sites may be a research type work that we're doing. This boils down to the state and local agencies that are doing regulatory work on these additional 250 sites. What can they afford to do, both in the laboratory, as well as by samplers?

MS. HERING: So,...

MR. MERRIFIELD: The economics impact, what we can afford to do.

MS. HERING: So, one thing that you might be looking at is, what are cost effective methods. This was on my list this morning, in terms of what's reasonable to do from a monitoring point of view, that can carry on beyond the super sites themselves. Feasible measurement methods for long term monitoring.

SPEAKER: I really have something to say now..

MS. HERING: Okay.

SPEAKER: I guess I'll follow up on that one. At the end of the day, this information that we've gotten. Health effects, and one of the people who will be working with the super sites, we need some directions as to how we prioritize. There are I call standard methods. For example the CMs, ozone. So, what we're looking for is direction as to which types,

prioritize this.

MS. HERING: So, one thing that we can do, and actually I planned to do it after we get some kind of list here, is to go through priorities and priorities measurement methods for the super sites.

SPEAKER: That data that we get, whatever it is, to do modeling or look at the health effects.

MR. TOMBACH: There's even more to it than measurement priorities. There's the question of how good do our measurements have to be. That's very important because we don't have the mega bucks around to develop method, improved time resolution to the nanosecond and probably nobody needs it to the nanosecond. So, what is adequate time resolution for health effects work. What are the adequate time resolutions for source receptor analyses? It isn't really seconds and it isn't 24 hours. the amount of money you spend on the problem is going to be closely related to what time resolution you really need. I think the same thing with accuracy, precision, lower detection limit, for all these parameters someone really needs to sit down and say, for the problems we're trying to solve, how good does our information have to be and that will help us prioritize where we spend our money on trying to make methods better. Right now we don't have that kind of structure. People are developing methods and

improving them as they, for their own individual needs. But here we have an integrated, chance to look at it in an integrated manner.

MS. HERING: I think these are, if time resolution, accuracy, precision, coverage is another one, spatial and also whether...

MR. TOMBACH: Even temporal.

MS. HERING: And temporal, whether or not measurements are made every day or every third day or every sixth day.

MR. TOMBACH: Or seasonal representative, as we heard today.

MS. HERING: How do I call that? Temporal, I'll call it temporal, I suppose, in addition to...and these questions probably need to be addressed, differently and probably different answers for different parameters here. There's no one set of answers.

MR. TOMBACH: And also for different problems. Health effects has a different answer than modeling.

MS. HERING: Yes. Yes.

MR. CHING: Jason Ching, EPA. Under these categories, isn't there data qualitative objective? You can have data quality objective for some sector, for health, for different things and that might be a way to organize the priorities. I remember

having to do that for...

MS. HERING: Basic data quality objectives.

MR. CHING: They call them data quality and all these things fall under that category.

MS. HERING: So, is there something missing here?

MR. CHING: Lots.

MR. DREHER: Just to address the one question. Kevin Dreher, EPA health effects. In terms of addressing all these 10 or so endpoints here, I think one thing that this group, or even other groups, health scientists, help you would be to prioritize them, in terms of what is the existing database that puts one of these distinctions at the top of the list versus the higher risk. There's really no health or laboratory data to, like peroxides, yes, chemically that's plausible, but I don't know any laboratory studies using ambient air particles that have really provided hard data to say this chemically can happen but it hasn't been tested in particles. So, I think in terms of prioritizing this list of measurements, would give you some direction in terms of what we'd like to know. For example, I've done a lot of work with metals. We'd like to know what metals are in the fine versus coarse fraction, how bio available are they. You're already measuring the co-constituents, so that's already covered. We'd like to see more

elemental compositional speciation, which gets to the bio availability issue. I mean you can do elemental speciation, but it's much more difficult to do the elemental composition speciation.

MS. HERING: You mean the oxides...

MR. DREHER: The oxides...

MS. HERING: The valence level.

MR. DREHER: ...the valence, and things like that. I think that's another area.

MS. HERING: I'm going to add, so you see valence states.

MR. DREHER: I would just put elemental composition speciation, which covers you know, oxides, sulfites and obviously with that the gases.

MS. HERING: Composition state. Oxides...

MR. DREHER: Well, I would just put elemental compositional speciation.

MS. HERING: Well, I'm, okay. It didn't mean as much to me, that's why I'm clarifying it, just for my own notes.

MR. DREHER: The health scientists can give you the list of 10, but there has to be some in terms of the economics of this. Which ones are the more plausible versus the higher risk things?

MS. HERING: Well, I mean prioritizing that list is not the job of this session here.

MR. DREHER: Sure. But I would hope the health scientists are doing that right now.

MS. HERING: I think perhaps what I'd like to do at this point, since we've sort of gone through a whole list, is to start with the parameters which are the most obvious, which are the major chemical constituents and then some of the physical size distributions and answer these questions.

SPEAKER: Can I add one more to the list? Calibrations, especially at the low levels. What is the routine process at the low levels?

MS. HERING: Standards for a specific aerosol species, is what you're after? Okay. Specific compounds at low levels, or appropriate levels.

SPEAKER: I have two suggestions for additions to the list. One is, that in talking about source receptor relationships, we haven't really focused all that much on direct measurements of loss mechanisms, deposition rates and so on. I think that to a certain extent that's in the vertical profile and I'd like to make it explicit, that we should be thinking about loss rates. Also for really serious primary emission of these super sites, the primary thing we're talking about, being related to health effects. I'd like to hear from the health people in the community what local, and in the

room, what local hospital data we might want to have collected, that are contemporaneous with the aerosol measurement. Should there be local hospitals for which admission rates are collected? If so, what type of data would be collected. That opens up a broader range of data analysis opportunities. People have hypotheses that they'd like to test.

MS. HERING: So, you're saying the siting of the super sites and the whole program, should be such that there is, the EPI base that can go along with it, in a broader statement than what you're seeing.

SPEAKER: That's right. And maybe that's implicit.

MS. HERING: Well, it never hurts to put these things down. If what we say overlaps somebody else, that's okay. Not only possible, but integral.

SPEAKER: Just to comment on that. I think at the end, this will be a point where this will start to dovetail.

SPEAKER: Missed the point on the loss deposition.

MS. HERING: Oh, I think...that's actually in, I didn't write it down, it's in the receptor write up, deposition rate. I didn't look at it as, I didn't list it as a measurement parameter, but it...

SPEAKER: But you can calculate

from size, you can also directly measure deposition rates. The deposition rates on various surfaces and something that could be a part of the sites.

MS. HERING: Yes.

SPEAKER: Yeah, I think there's an important point on this one, what Jason and I made, and that is that we're not concerned with trying to quantify the resolution, but desirous of specifications for that.

MS. HERING: Yes. There isn't, well, actually what I was interested in, was to take some obvious parameters that we know are going to be measured and get input here as to what time resolution, what accuracy precision, what spatial, especially these two, because they're so method dependent, spatial and temporal. They're also to some extent naturally dependent. What do we feel are reasonable goals that we should be reaching? This is, presumably people here in this room have either measurement expertise or they're from the health or source receptor community and they have real needs. The whole point is for us all to talk. So, if we look first, first of all I thought we would look at the so called routine chemical speciation. In other words measuring the inorganic ions, the sulfates, the nitrates, the ammonia ion, the organic carbon and soot or black carbon content of PM2.5. Just sort of starting with that measure, I mean the proposed speciation sites, measurements every third

day, 24 hour integrated measurements. Is that sufficient time resolution? Do we need better time resolution involved?

SPEAKER: You're going to need three columns here. One column is for regulatory purposes, like trends and such. One column is for health effects work and one column is for source receptor work and they're very different answers.

MS. HERING: Okay. We'll just make three columns.

SPEAKER: Maybe more, but I think three at the moment.

MS. HERING: Okay. Regulatory, health effects, source receptor. Is that okay? I see lots of source receptor people, should we start here. In terms of time resolution that would be desired.

SPEAKER: I'll offer no more than 12 hours.

SPEAKER: It depends on the model. You really don't want to go more than three hours.

SPEAKER: I think you're too much limited by present technology. The question is, if we had the choice of...

SPEAKER: Continuous.

SPEAKER: ...no, no...of doing it right, but we don't want to spend any more money than we have to, what's the optimum number?

SPEAKER: What I'm saying is, based on the history, that's the way people do.

SPEAKER: My statement to you was, for emission based models, the trace receptor model.

SPEAKER: You can do 24 hours too. It really depends.

MS. HERING: If you had 10 minute data, what would you do with it?

SPEAKER: If I had 10 minute data, I think it's a lot of headaches.

MS. HERING: More than you need.

SPEAKER: Right. Hourly is probably pretty good.

MS. HERING: You would probably average it to an hour?

SPEAKER: Yeah, an hour is probably easier to deal with.

SPEAKER: Plans to put ecological data in that.

MS. HERING: Three hours. So, you're looking more at this number.

SPEAKER: We're using three hours.

SPEAKER: We do hourly mostly.

MS. HERING: And you do hourly. So, we get a circle.

SPEAKER: For mechanistic models you really need an hour resolution. Meteorology

changes too fast for you to do anything other than that. But for source receptor, for receptor models I guess it could be longer.

MS. HERING: What about for health effects? You health effects people here in the room.

SPEAKER: How about epidemiologists?

MS. HERING: We're supposed to have a mixed group. Don't tell me everybody here is a measurement person.

SPEAKER: We use two hours.

MS. HERING: You use two hour measurements in Europe.

SPEAKER: Yes.

MS. HERING: This is ambient exposures, ambient air. I think, you said you've done...

SPEAKER: It depends on, I guess the six day thing is not good obviously. The three days, if they can get 24 hours, 12 to 24 hours, obviously they would like to get with interface source receptor, if they can get that, they'd be ecstatic, but I don't know whether they can do that. So, to me I think that these six to 12 hour times frames...

MS. HERING: You're thinking six to 12 hour. What I believe I heard from epidemiologists that the most important thing is to have at least some measure every day.

SPEAKER: Yes.

MS. HERING: At least daily. At least daily, no gaps. This is of less importance.

SPEAKER: Probably it would depend on the particular measures in the study. If they're doing a huge study and they're doing some sort of physiological measurement, that they can take once an hour or something, then they might want hourly data. But a lot of the data would be just once a day. So, it's probably a lot better to have the hourly resolution.

MS. HERING: So, for the long term exposure types, EPI studies, the most important thing is to have an uninterrupted database. Not so much what the time resolution is, but to have it uninterrupted.

SPEAKER: For human exposure work, aren't you interested in activity patterns? Activity is going to depend on time of day and it will be very episodic.

SPEAKER: If you're looking for ultra fine particles, these things come no farther than 50 meters. You need a time resolution of half an hour, or otherwise...but if you aren't, there are uniform. If they are not uniform, you better check your operator. It means that 24 hour measurements to find if you have to look for what you're after.

MS. HERING: So, it depends on the...I'm looking at the routine chemicals, looking at

that species. I mean we could, I was going to go through and ask these questions also for size distribution, C&C counts, particle size distributions. Is that going to, I have the feeling I'm going to elicit the same answer. But is that true? If we add, that's a measure of the particles below the 10th micrometer and the number and concentration of those particles. There's also surface area measurements. That's something that I've heard an interest expressed in by some health effects people, although it's not on this list. Maybe it's implicit under ultra fines.

SPEAKER: Is number included in the health?

SPEAKER: I think the ultra fine is the physical parameter.

SPEAKER: So, it's implicit.

MS. HERING: So, it's implicit. Here you want number, surface, maybe just total size distribution. From a regulatory point of view, once every sixth day, is that what it is? Depends on...that's for mass.

SPEAKER: Could be every day, could be every third day.

SPEAKER: Depends on what kind of receptor it is.

MS. HERING: So, from one to six days.

SPEAKER: That's what the regulations say, that isn't necessarily what they need.

MS. HERING: What do they need for their implementation plans, which is...

SPEAKER: What I meant, but they may not be what they necessarily need for, to do it right technically. It is rather what the Federal Register says, thou shall do.

MS. HERING: Yes, if we get, if we step back away from the Federal Register, that's the opportunity here and we say, from a regulatory point of view, measurements at these intensive sites, through the speciation network and the super sites are in part, one of their purposes is to support state implementation plans. This means that not just, let's go around, but if we're looking at measurement methods in the future, what sort of measurement methods would we like to have validated, so that state implementation plans can be refined in the future, when quite not so many resources are available for measurements. So, we're looking at ideally time resolution on the order of hours. Is that a fair summary? Accuracy and precision, here we have...I should separate these two. Accuracy being, precision is not so hard to define.

SPEAKER: That item I don't see how this group could answer. The answer is different for every single item on your list there.

MS. HERING: Okay.

SPEAKER: Then you still need the three columns.

MS. HERING: Well, let's see, let's, I mean we can go through it by constituents. Sulfates, nitrates, organic carbon, organic elemental carbon, C&C counts, surface area, surface size distribution.

SPEAKER: You're looking at it like an aerosol physicist. How about the accuracy and precision of cloud and fog presence? Which is a burning question in a number of studies right now. In fact it probably controls the answer. Burning is not a word I should use now.

SPEAKER: You're referring to location and depth, right?

SPEAKER: Referring to the presence of clouds, does a plume go through a cloud type of thing and if so, what are the properties of the cloud it went through.

MS. HERING: And how in the world do we measure that?

SPEAKER: Right, yeah.

MS. HERING: If I understand the source receptor, this is something that needs to be characterized, for secondaries especially. I see the accuracy issues relating to validation and comparing different filter methods or whatever.

SPEAKER: The question we're asking here, how accurate were the measurements to be used.

MS. HERING: Maybe perhaps what's reasonable, what do we feel is a reasonable goal.

SPEAKER: Well, I think you ought to ask for a first question, what do you need to answer the questions you've posed to yourself and then ask yourself whether it's reasonable or not.

SPEAKER: What are you going to use the data for? That determines the answer to the question.

MS. HERING: Okay.

MR. ALLEN: I think the more...Dave Allen, University of Texas. I think the more basic question is, what do we mean by accuracy. Do we mean by accuracy what was present in the undisturbed air mass? Accuracy performance in some standard that we might develop? Do we mean as accuracy, an accurate reflection of how this air mass might behave as you inhale it? I don't think we know what we mean by accuracy.

MS. HERING: I think I'll go to the next page for accuracy here. Okay. I'm just going to put these numbered things up here. So, accuracy issues first represents what is airborne or is it against a standard or is it reflect what you read. Is that what

you had?

SPEAKER: I think that we can't answer that question. I think we just need to say it's not entirely certain what we mean by accuracy.

MS. HERING: Well, if we stick with the first two...

SPEAKER: We could spend the whole 15 million on defining accuracy.

SPEAKER: Exactly.

MS. HERING: Yes.

SPEAKER: Depends on the integral of sampling also.

MS. HERING: Preparing...

SPEAKER: Higher accuracy because the sample contained method is not what you're looking for, there's also the detection limit.

MS. HERING: But also if you composite short samples, presumably the answer doesn't depend on your sample duration. It was an old trick in evaluating methods, when they were first, when they first came out.

SPEAKER: I'd like to ask a question.

MS. HERING: Yes.

SPEAKER: Peter phrased it very well this morning on aerosol water and it relates to accuracy. Is water, in aerosol form, an artifact for the health effects people or is it a component of the

aerosol that is going to create a health effect? Because it makes a big difference, if you're going to eliminate the water consideration in the mass or in the chemistry that goes on in the filters. Accuracy then is going to be dependent upon accurate relative to what water is on it.

MS. HERING: Yeah, I see that.

SPEAKER: It's going to be critical.

MS. HERING: So, the whole issue of, well, the mass as it's defined, because of the relative humidity equilibration, is not factual mass of what's suspended in the air.

SPEAKER: Well, worse than that.

MS. HERING: So, if you're talking, I mean this is like comparison of mass, there's comparison with the standards which would be the reference method presumably.

SPEAKER: Well, it's even worse than that. In the case of the federal reference method for eastern sulfate and aerosol, where it's non neutralized ammonia sulfate, it is being neutralized as time goes on, while it is sitting around just picking up ammonia. The amount of water it contains at this 30 to 40 percent relative humidity is changing from day to day at the same humidity, as the neutralization state is changing. So, your answer is non unique. There's some fun stuff here.

MS. HERING: So, there's the whole question of what is the federal reference method measuring.

SPEAKER: It really makes a big difference. Because if we're going to do source receptor model evaluation, we have to know what the measurement is, first of all for models of predicting unequivocally and we don't have a clear definition of what the particles are at the point of sampling versus the point of storage and etc. So, it's very difficult to match the two. So, it's a real problem.

MS. HERING: So, what you're saying is, in terms of defining accuracy of measurements or even defining measurements, knowing what's there in the federal reference method and what parameters influence what is measured is very important to know how the measurement relates to what's in the air.

SPEAKER: Yeah, not only the federal reference method, but you're dealing with mass alone. But into the more research, more health...

MS. HERING: How does any measurement relate to what's in the air? That's really this one. Well, we've had a lot of sort of general, I mean some specific ideas, specific things and some general comments and I'm trying to think now how we might get back to our charter here. Oh, precision. It's getting hot in here. Well, precision is often defined by

co-located sampling. Well, there's the sample too. You have a sampler operator.

SPEAKER: It's hard to figure out how you could separate precision and sampler from the operator, unless you're going to do multiple operators in the same sampler.

MS. HERING: I've heard of that being done.

SPEAKER: You can do it, just the way you said. You have 1,000 operators across the country and just take all the data and compare it. You can see where some of them are coming from.

MS. CLEAVER: I'm Candace Cleaver, Washington State University. The sampler precision is going to be important I think as these super sites get set up. For example, in the volatile, the semi volatile organics sampling, right now the organic sampling that's done, when they do elemental and organic carbon, these were filtered, the federal reference method uses a Teflon filter and they have different, you won't get the same organic carbon number if you put a Teflon filter along side the organic filter. There's some difference in the collection there. That's when your precision question is, or an accuracy question is, a certain amount of bias.

MS. HERING: So, organic sampling.

SPEAKER: I think people define

precision in different ways. If you go out and make a measurement and fine on thing, then the precision could be different.

MS. HERING: So, there's the question of definition for cross comparison. Precision depends on the concentration level, that's true.

Well, let's get back to, we've got accuracy questions. We listed a lot of things that might be looked at, at the, I think at the super sites and I think we shouldn't limit ourselves to super sites. There's also the speciation sites, which there may be, since these things are not yet set in stone, there could be varying levels of super super sites and then super speciation sites, which are somewhere in between. This is all possible, I believe at this point, depending upon recommendations. We have, I mean I think from a practical point of view, if we're to look at future needs for health exposure and source resolution and accountability, what we've so far tried to look at, what parameters, a list of parameters that might be, that need to be considered. We've talked about time resolution. We haven't talked about organics characterization and if the, I mean we proposed in the draft paper that comparison of different methods of characterizing organic fraction, even just question with regard to what you call organic carbon and how you say what's in that organic constituent, which is such a mix

of compounds, is questions, was posed in the draft comments. It's a question that should be addressed at the super sites. We have comments on that. Any ideas about what might be more specific?

SPEAKER: I think we need to move beyond the operational OCEC split type of thing. That's causing us, I think as we understand more and more what's involved, more mischief than is good and need to start facing the reality that there are multiple species involved and somehow or other, develop some sort of way of classifying those species into a minimal number of groups, so you don't have a thousand answers every time you do it. I think we need to face up to that issue that we need to move onto that next level of detail.

MS. HERING: Perhaps marker compounds?

SPEAKER: That's a possibility.

SPEAKER: Compound classes.

MS. HERING: Compound classes, that sort of species. We can say it two different ways, it's okay.

SPEAKER: There was recent workshop, different experts in the field, and their conclusion was to, they recommended starting out with this general subclass to work on and then moving onto into speciating those as technology became available. So, it was along those lines. But it is, I guess what I'm

saying is it's already in the process. It actually went quite a ways in terms of identifying the needs.

MS. HERING: But is there consensus that this is a need that should be addressed in the super sites?

SPEAKER: Absolutely.

MS. HERING: High priority, okay.

SPEAKER: That's need #1. Need #2 is to deal with the VOC versus particle carbon split issue, the whole question of which we heard today, one solution is, forget that and go back to the dark ages and that's one way to get an answer. But someway or another we need to resolve what do you do with the back filter. Do you add it, do you subtract it, should you use it or shouldn't you, those are critical.

MS. HERING: So, overall related sampling issues. Does that make sense? Does anyone know of, since the sampling methods tend to be long term, does anyone know of any sort of promising methods out there, that might be looked at for a higher time resolution measurement of organics, with something? Well, OCEC we can start with. I mean there is a commercial method out there. But are there comments on whether or not...

MR. ALLEN: I'll throw something out, which is, traditionally in the organics...Dave Allen, University of Texas...traditionally in the organics,

we've relied on mass spec, maybe a little bit on IR, but there are whole classes of analytical measurements that really we haven't applied at all. For example, the recent development in carbon 13 in mass spectroscopy. I don't think it's seriously been applied to the problem of characterization of these materials, which might help get around some of the mass spectroscopic problems. So, I think that there are a whole class of analytical tools, that we really haven't explored.

MS. HERING: These are for filter samples or...

MR. ALLEN: Well, for example with NMR you can make measurements on solids, but easily on extracts.

MS. HERING: Okay.

MR. ALLEN: So, at the same time you're doing a lot of these other workups for GC mass spec, looking at polar, non polar compounds. But that gets back in my mind to the issue of sort of opening up this problem to a much broader community, by having available archived samples and standards and other things that would allow people to test things, without making the huge investment of going out to a super site, becoming a field sampler for air quality.

MS. HERING: So, archived samples for testing by multiple methods, multiple labs, even if that sample isn't yet per se' exactly what was in the air,

at least you get to compare different samples on something that's close to what was in the air, among different laboratories and different analytical approaches.

MR. ALLEN: I think it needs to be done. Of course it has limitations that a particular method may require to be collected in a certain way.

SPEAKER: Coarse filters is a usual way for collection.

MS. HERING: I like this very specific recommendation with regard to a real problem. Related sampling issues, this is an analysis issue. Any ideas on getting time resolution?

SPEAKER: Big samplers.

MS. HERING: Okay, let's go, this is organics continued. What about impacted collection, as opposed to filter collection?

SPEAKER: Well, certainly if you look at the nitrate results that you showed this morning, the difference in technique presumably was because it was not done with the factors that occur with samplers. To a certain extent the same may be true for organic sampling, but it's somewhat more difficult to show that, again for all of the reasons that we've been discussing.

MS. HERING: Then there's the neuters. So, we're looking at collection methods as well. Organic collections, all of these things here.

SPEAKER: How about the particle concentration?

MS. HERING: The organics is sort of a, the worst case example of our particle characterization, chemical characterization issues. You're dealing with the semi volatiles, you're dealing with positive artifacts and gas absorption and you're dealing with something you can't characterize chemically. So, I think if we go through this one, we've got what we need for the nitrates and the sulfates should be a done deal.

SPEAKER: Are we trying to establish a list of research needs here relative to organics, or are we trying to establish a list of things we would recommend that would go on a super site? We've already identified that the things that are not ready as they progress to go to a super site for demonstration purposes. A number of these things we're talking about, I think fall under that category. I think we all realize there's a lot of needs in the area of expanding our ability to make these measurements, but is that what we want to accomplish in concentrating on here, or is it more what's out there now that we can be looking at to, as the first round, as far as methods?

MS. HERING: I was taking the question, I mean correct me if you think I'm wrong, as the former rather than the latter, because there are

other groups, the groups on health assessment, some personal exposure and source receptor relationships, who presumably are making a list of measurements, based on what technology is currently available. That should be the core of these, a core program for these super sites. What the charge of this committee was, was to look at field or aerosol measurement issues, I think as relates to the future. Also to look at those as relates to characterizing the more standard methods that are being used, one of which is the reference method. That's something we haven't touched on, that perhaps we could, if this is appropriate, we could move onto that.

SPEAKER: So, you think the other groups are coming up with measurement methods, or coming up with species that need to be measured?

MS. HERING: No, they're not really coming up with, they're coming up with things that need to be measured. Our task...well, we can certainly put input, if we'd like to discuss that, we can certainly do it. It wasn't, it's, our task primarily was to look at validation of methods and this validation of methods and raising questions that needed to be evaluated in the field, both with the look to the future and with the look to quantifying, better quantifying reference method and I think quantifying chemical species methods. It wasn't explicitly listed, but it's certainly going to be

such a core part of measurement programs and should also be here on the list. As for whether or not we want to really take a stab at recommending those methods here in this room, I don't know that that's so much our job, as to say what, how they should be done.

SPEAKER: I think inevitably there's going to be an overlap between the sorts of things that we're discussing here and the sorts of things that are being discussed in several of the other groups. I think that however the difference is that they're each intended to approach these questions from different points of view. As I understand it, our job should be to approach measurement methods from the point of view of what we can do and what we think we might be able to do. Then the health people should approach it from the point of view of what we think is needed to answer hypotheses, that we think we would like to test. Then we put these lists together and find out what the intersection is.

SPEAKER: Possibly focusing species, possible problems in measuring those species and possible routes to solving those problems and not worry so much about why we need to measure those species. I mean that's obviously important, but I don't know that that's our job.

MS. HERING: Okay. Chemical species, the health list is still a little bit general and I

think perhaps, I mean the list, the first thing on the list is mass. Well, there's, I mean that's going to be done by the parameters.

SPEAKER: Okay. We just threw science out the window by saying that. FRM provides one measure of mass, but it is a biased measure of mass. The question is, do we want to accept that for the super sites, or are we going to want to measure mass in a way that's more consistent with all the other techniques we're using? In that case we have to deal with the biases.

SPEAKER: You need to approach that within the time frame of the things we talked about earlier, like the time resolution and things like that. FRM is a 24 hour measurement. So, what would be recommended to approach the shorter time interval, what exists out there.

SPEAKER: Well, you can have the TM or the Beta system, that's the two that I'm aware of, there might be more.

MS. HERING: Surrogates. There all kinds of other surrogates to look at actually.

SPEAKER: And they come with their own biases.

MS. HERING: So, I'm going to say time resolved methods, and there's a whole list of these.

SPEAKER: But I think one thing is for sure, I mean, I think you have to be, you can run all sorts of other methods, but you need to run the FRM as well. You can't not run that one. You need to be able to reference everything back to that.

MS. HERING: What about doing chemical speciation on FRM samples to compare, for instance the nitrate on an FRM sample versus what's on a filter method?

SPEAKER: Don't bother.

MS. HERING: We've got don't bother and it has to be done.

SPEAKER: The purpose of the super site is to document the problems with the FRM and you've got to make measurements like this.

SPEAKER: I guess the first question we ask is, is there anybody who thinks there's a method to measuring mass without bias. If the answer is no, then we can list all kinds of methods and I think we should just move on.

MS. HERING: Okay.

SPEAKER: Because we know what needs to be done.

SPEAKER: You know, most of the biases that you've thought about here have to do with what happens when you collect the particle. You have interactions of chemicals, semi volatiles and particles.

But if there were a way to directly weigh each particle in the air mass, for example, and add it up, that would presumably avoid that class of problems, but inevitably introduce other problems having to do with that. But I think we should be considering a range of techniques, not just techniques that involve collection, but groups that have other kinds of problems and directly reconcile.

SPEAKER: I think what you said earlier in your talk, the key point is that the best way to get, to approach truth, is by comparing methods that use different physical characteristics as the source of measurements that you can try and hypothesize as to what's really going on. One of the things, as far as methods with the super sites, this gives us a chance to be able to develop a citing where we can co locate and derive these different types of methods, where we can try and come up with some fundamental analyses, where we can try and assess what truth means or what accuracy is.

MS. HERING: This was actually the point of the slide I showed too. Comparing methods that have, from first principles where one would expect to have different biases and to see how closely they agree, to see how much they're giving some idea. I've listed here all the things I can think of that give time resolution on the aerosol as a whole, that can be

interpreted in something close to mass. Beta gauge or tapered element mass balance, measuring complete size distributions, which can be with OPC, optical by optical patterns, genetic particle size, DMPS stands for differential mobility particle size, QCM, pressure drop and there's the electrical impacted too.

SPEAKER: The electronic cascading.

MS. HERING: The charged particles you measured.

SPEAKER: Particle analyzer.

MS. HERING: This is also charging and looking at...

SPEAKER: Mobility.

MS. HERING: ...mobility, yeah.

SPEAKER: By vibrating it and then the other one, the versatile, there's a variety of different types of field acoustic and electrical.

MS. HERING: What's it called? I'm not familiar with this one.

SPEAKER: It's brand new. Versatile particle analog.

MS. HERING: Okay. I'm going to put your name down by this one.

SPEAKER: Okay. Doesn't come out of the 15 million. We shouldn't sell old fashioned weighing totally down the drain. I mean the point is, it may not have very good time resolution when used with

a low flow rate measurement technique, like the FRM for that matter, but if you use a high flow rate, you can get good time resolution.

MS. HERING: We could put down here also volatilization barometric mass, right? Well, no, what I mean is you look at the nitrate on your filter, on your Teflon filter that you weigh and you look at what you get by another filter method. If you trust that and you look at the difference and you add it back in as ammonium nitrate. That's a standard technique in California. So, there's mass issues measurements with differences, there's calibration issues with the real time instruments and the question is whether or not, you know, with proper calibration and careful application of these methods, whether or not some of them agree or not, under a variety of conditions.

I'm going to go to the next page for ions. Any further discussion on mass? We've got a nice list.

SPEAKER: I guess the only thing that I might suggest is that if I wonder if it would be useful to categorize the various measurement techniques that we discussed versus integrating techniques?

MS. HERING: I think that's useful to look at. Well, all of them, are there any true ones that don't, there are some that sample the air, but look at the particles while they're still airborne. That would be

all of these.

SPEAKER: That's about the closest you get to an unaltered aerosol. It's a hundred odd some liters per minute going through a big open door.

SPEAKER: In talking about mass measurements, I'm a little uncomfortable talking about methods, which is very much secondary. These are measurements and I know there's a correlation between light scattering and concentration, but you get that correlation with a filter measurement. But it can be calibrated with atmospheric particles of known size.

SPEAKER: No.

SPEAKER: Yes.

SPEAKER: I absolutely disagree.

MS. HERING: How about if we call this mass and surrogates? Actually the reason, one of the reasons I put that up here is because it's been mentioned over and over again as a real time surrogate for particle mass measurement. You hear that over and over again.

SPEAKER: It was proposed in the Federal Register as a Level III method.

MS. HERING: So, it kind of has to be on the list.

SPEAKER: It is one of the endpoints that we're after, feasibility, at least in some areas.

MS. HERING: We have filter based

methods and the neutered filter methods. We have real time or automated I'll call it, continuous or semi continuous. Filter based, Teflon filters and coarse filters for sulfates. Now we have to get by species. Okay. Sulfates, this has got to be the easiest, right? Okay. Let's start with sulfates. If you're looking at filter based, sampling on Teflon or coarse, right? Some people sample on nylon actually, right?

SPEAKER: Need to put a question mark by nylon. People do do it.

MS. HERING: Actually here's another question. If so much of the speciation network is done on improved samples, do we want to have cross comparisons between improved and speciation samplers?

SPEAKER: Yes.

MS. HERING: Yes. So, improve the speciation samplers, by that I mean the EPA procured one, the one in the EPA procurement. This is already going to happen. This should be done and we would, or you already have recommendations on the number of cities. Should it be done as an ongoing thing, as part of the super sites or just be done once and will we recommend some comparison as far as super sites?

SPEAKER: Well, there's an initial evaluation that's going to happen with that.

MS. HERING: Okay. Nitrates...oh,

we didn't mention the impactors, I didn't finish the list here. Impactors. Single particle. Real time. We've got, there's alloy based methods, there are other...

SPEAKER: When you say single particle, you're referring to...

MS. HERING: Oh, that's the old, old method by difference of S02.

SPEAKER: What about ion chromatography?

MS. HERING: This one has time resolution, I think with minutes. Ion chromatography is about a half an hour.

SPEAKER: I think the on line chromatography is down to less than 10 minutes.

MS. HERING: Okay. Nitrates. We have additional questions on the neuters.

SPEAKER: Do we all feel those are pretty good methods for doing it, or does anybody have questions to look at?

SPEAKER: Wouldn't recommend nylon with the sulfates.

MS. HERING: That's why this question mark is here. Oh, are we recommending that. That was on the list because people do it that way and it was for purposes of quantifying the errors, I think. Is that fair enough?

SPEAKER: I see on line

chromatography methods, but wouldn't it be possible to just take the filter, the Teflon filter out of the unit after 24 hours and extract with a known amount of water?

MS. HERING: Yeah, that's what this is.

SPEAKER: Okay.

MS. HERING: On line chromatography is where they have a chromatograph there in the field and they use a different method of pouring it directly into the liquid.

SPEAKER: Okay, now I understand.

MS. HERING: These are sort of more or less automated real time measurements that look like they're ozone analyzing. Okay. Nitrates. Who will start it off? Just list the obvious ones. Nitrates you can also see by...

SPEAKER: It's not quantitative. It may or may not be in the future.

SPEAKER: I think particle mass spectrometers will become more quantitative in the future.

MS. HERING: We have an authority here. She wants it on the list.

SPEAKER: Near term versus long term objectives.

MS. HERING: Okay. We're getting confused again with, I should put down what are

recommended methods and whether they're tested methods.

SPEAKER: One in addition to sulfate, as well as for nitrate, is both impactor based and real time based IR methods for sulfate and nitrate.

MS. HERING: Sort of the impact IR methods.

SPEAKER: Right, you can do that in real time.

MS. HERING: There's some real time nitrate models. There are actually a surprising number of questions that came up in the meeting about differences in techniques and comparison of those that are at issue.

SPEAKER: That's an issue that needs to be addressed.

MS. HERING: Comparison to different filter methods.

SPEAKER: I guess I'd like to raise the question Paul raised for sulfates, which is, do we think we can make a good measurement of nitrate with these methods?

SPEAKER: Depends on time resolution.

MS. HERING: Depends on time resolution. So, we have real time nitrate monitors, on line chromatographic methods.

SPEAKER: The rotating continuous.

MS. HERING: That's analyzed on line also by ion chromatography, is it not? Well, whatever they are.

SPEAKER: Do the real time techniques use the neutered with the nitric acid first?

MS. HERING: Probably depends. I think they all do. It might be an easy way to check the neuters. Overall difference, should I call it?

SPEAKER: Yeah.

MS. HERING: Do you know how the wet to neuter one is analyzed, is that also by IC? Okay. So, these impactor collection, impactor ion, needs to be listed back in the sulfates as well. Do we need, as part of super sites, laboratory comparisons? I don't think so, I think it's pretty well set. That's pretty much a done deal, I hope.

SPEAKER: There definitely needs to be comparisons between the species that go to a lab for analysis.

MS. HERING: I think there are, having run a number of comparison studies, you can make a list of things and then when you talk about comparison studies, you have to be very careful and you break down sampler, operator, laboratory and you try, and you devise the experiment in a systematic way so each of these components is tested separately as

much as possible, as well as different test on the whole integrated thing, with different sampling periods and so forth, protocols. Protocols are very important for method comparisons and field validations. I believe they have to be carefully thought out. Having stated an opinion, which I'm not really supposed to do, do I have any comments on that? Organics we already talked about. We haven't really talked about carbon measurements.

SPEAKER: They claim elemental carbon and hydrocarbons.

SPEAKER: Are we interested in ammonium?

MS. HERING: Ammonium. Mass spec on here. I didn't recommend them. I mean there's a number of, we'll probably get as many opinions as there are neuters out there. I just put it down as something that probably should be looked at. I think ammonium, I don't know of any real time ways of doing ammonium ions. But would it be good?

SPEAKER: There's a real way to do ammonia and it seems like we could figure out a way.

SPEAKER: You can do it.

MS. HERING: So, I'm going to put...should we say real time is needed? Is that fair enough, or do you feel it's not an important issue?

SPEAKER: I think it is, in terms of

the acidity.

MS. HERING: Pretty much the same as you heard for comparison. You could do it on impactors, but real time.

SPEAKER: I assume we're making a laundry list of all these different methodologies to be measured. If we do a particular metric, that we would, these measurements at however many super sites there are, you'd want to make the basic measurement and I assume it's the baseline and would probably be something like whatever this speciation network and be the baseline involved. These other methods, because of time resolution, one or two of them you might want to evaluate or maybe all these various methods that would certainly be something that wasn't designated at all with the sites. There might be one super site facility where you can do all the method evaluation and then you would rotate around for comparison. But I just hope that we're not going to the idea that we're going to try to put all of this equipment at every single site, while we're generating this list of methods. Again, you don't want to lose site of trying to support EPI and all these other things.

MS. HERING: So, well here, I think maybe this is an important point. How many sites, how many seasons? You're saying one site, I can see arguments for going to at least a site that's very

different.

SPEAKER: He didn't say that, he said one site and then going onto another site later.

MS. HERING: Okay. So,...

SPEAKER: I don't know if it would be cost effective with all the things you want to do, to try and...

MS. HERING: Do them all at the same...

SPEAKER: ...do them all at the same time. So, maybe the baseline method.

MS. HERING: I think it's an excellent one. Doing rotating comparison sites. So, there's the need for standard samples. For the analytical methods, the question comes up again as always, the collection. Taking, going back to Dave's suggestion about, for instance if you want to compare.

As they become on line, if there's more than one, or even so just targeting this is something that needs to be done, as a field test, just to see how it works. Even if you don't have a cross comparison for the oxidation state, compare it with the elemental composition. This is a research area, fair enough?

SPEAKER: Yeah.

MS. HERING: But it's important.

SPEAKER: Might be.

MS. HERING: Maybe. Okay.

SPEAKER: I think we need to talk about some simple straightforward things that can be done and should be done at each super site.

MS. HERING: With regard to methods?

SPEAKER: With regard to analysis of the total elemental composition and the soluble composition by ion chromatography and the soluble metals or some other analytical method. In other words, I think most people would agree you need to know, you've got this filter sample here, obtained by FRM or some other method, but for sure you're going to have one from the FRM, how do we analyze the ions and the elemental composition and the soluble ions in metals in that. Is there some protocol that we should all be using just to get that information? In other words, if all 50 super sites are going off doing it 50 different ways...

MS. HERING: We're not talking about that. We're not addressing the 50 sites. Addressing the inorganic ions, the elemental composition in terms of XRF and oxidation state. Water soluble metals, I don't think is in there.

SPEAKER: We're not segregating this to programs.

MS. HERING: Okay. I stand corrected.

SPEAKER: Is there some, should we talk about some generally applicable protocol that most of these sites should be using?

MS. HERING: I'll say, why don't I put it down here as something to come up. I'd rather not take the time to do it.

SPEAKER: A basic issue that Kurt is bringing up, an initial role for the super sites be an inter comparison study for what we regard as being the major target species. Go down the inorganic ions, go down OCEC, should it be an inter comparison study in preparation, should that be the first year of the super sites, or should the first year of the super sites be more broad based measurement? I don't know that you'd have the resources to do both.

MS. HERING: I think, I mean my own opinion is that if you're going to do comparison for the major analytes, actually one reason I started there, I think it would be foolish not to put in the real time methods at the same time, because the expensive part of that, half the expense is getting the manual methods for comparison. So, I think it would be good to do that. But the basic idea, whatever is needed beyond what Paul is doing in the speciation network, correct?

SPEAKER: I know what I'm doing.

MS. HERING: We have general applicable methods comparison to all the major

analytes, as a role to the super sites. Is that, does that sound...it needs to be done somewhere. It's an objective, so that's a given. All right.

SPEAKER: Will that be done in time to have a major impact on the 50 speciation sites?

SPEAKER: We have the possibility of going out and doing a super site, where we could do some of the same for the next year. But the problem we have is, a lot of the selections have been made for the speciation methods and what we really need to do is compare them and see how they perform. They're using the same types of technology they've used before, but they're different on some points.

SPEAKER: I'd like to, I'm in a struggle with what the product of this discussion might be. So, let me just throw out some thoughts. Let's imagine for example that we were talking about the measurement of gas phase species, that are regulated. We talked about S02 and the conclusion I think would be that well, for continental situations which we're talking about for the most part here, that's pretty well under control I think. Even for the five year goal, we'd say we don't really need to work on that, that's not a high priority and we do the same thing for ozone, but we might say for intermediate species or for certain radical species, well, we'd like to have more routine measurements of these. Now suppose we do the same

thing for particles? Suppose we look down the list of species that we're dealing with? I suspect that there is no particulate species that we would say, for which we have no five year goals. I think we'd like to improve our measurement capability for every one of these. We'd like more real time capability. We'd like to be able to do it at lower cost and so on. So, I'm kind of wondering if it wouldn't be useful to sort of think about a matrix perhaps, where the first column would be the list of species that you identified in your first slide, and perhaps subsequent columns might be some sort of a synthesis of the state of the art, including major problems and the next column might be, let's say a five year goal and maybe a 10 year goal. I'm trying to imagine what might be helpful.

SPEAKER: I like your idea, Peter, but maybe along the columns of that matrix we would have whether we could do the measurement at all and how far along the spectrum we are to a real time insitu measurement so that we could say, rather than just saying okay, this is where we are, here's a five year goal, to really see where we are with the different methods.

SPEAKER: It's just a suggestion, but I kind of feel that there's so many things that we've talked about, that it's going to be difficult for you...

MS. HERING: To synthesize it.

SPEAKER: ...to synthesize this all. I just wondered if that might be valuable.

MS. HERING: So, we have...yes, I like this idea. Anything to make my job easier, right? So, we're talking about species and then you're talking about...

SPEAKER: The first column would be species and the second column would be steps, including any problems. So, you don't have to say anything else. How would you do it, David?

SPEAKER: I'm sorry?

SPEAKER: Instead of the five year goal, which you think in terms of...

SPEAKER: I was thinking more along the lines of where we are in the continuum, where the end of the continuum is real time insitu measurements.

SPEAKER: But is that a desirable goal? Do we really care, do we really need real time insitu measurements from any of these variables, or are we again starting to throw money at a problem that doesn't exist?

SPEAKER: For some things we said 24 hours is good enough, for other things we said one hour is good enough, that we wouldn't know what to do with 10 minute data. So, we need to figure out what is our endpoint again.

SPEAKER: But isn't that in part

defined for us by some of the other groups? We can at least characterize perhaps where we are right now. Maybe we're not going to say what an appropriate endpoint is, but that certainly is one possible endpoint that we could get to.

MS. HERING: Let's try it with something that we know something about, nitrate. Let's see how we do in this, all right. We've got status and problems. There's filter methods, there's impactor methods and there's, you've all been real time methods. We have for the filter methods we have good comparisons in some locations already, comparisons have been done. The results are variable, I would say. The real times are generally for the most part not tested, not fully tested.

SPEAKER: By validation I guess you mean evaluation of specifying the quality of the data. I don't know what validation means otherwise. You want to say they're true, they're useful or not useful, but usefulness is a perspective of what you want to use it for. Instead of using the word validation fundamentally, especially for a workshop like this, you should come out with evaluation, and what the objectives that would be used to specify the quality of the measurement, with respect to various bacteria. The users have to decide whether to follow this.

MS. HERING: So, we've go here what

I was, this was all, in this case I was just trying, this is all under status. I hadn't gotten to actually filling out the field evaluation, I just ran out of space. But I would say where we have issues...

SPEAKER: The question is very simple. We would like, what we would need is depends on what it is you're dealing with. If you're dealing with secondary material, in other words material made in the atmosphere that changes in concentration as a function of atmospheric dynamics or physics or chemistry, you need minimally less than 10 minute time resolution to understand where the stuff is coming from, because there's no way that you can sit on the ground and make a measurement without looking at the dynamics.

MS. HERING: Let's go back to our time resolution. So, we're now down to 10 minutes here.

SPEAKER: You also need, in many of the sectors, irritants from a health point of view, you probably want minimally an hour time resolution. So that you can understand the peak concentrations that are going to be inhaled, because it's likely that the peaks, especially for irritants are doing the damage rather than the averages, and this is what the health exposure workshop is for.

MS. HERING: Yeah, we had gone through earlier a list of time resolutions. We had only

gotten ourselves down to one hour though.

SPEAKER: But you might break that down to source receptor, understanding that was what the process is.

MS. HERING: But that's source receptor. I say secondary is 10 minutes.

SPEAKER: That's needed to develop...I think we've just created two categories. Source receptor for application and source receptor for developing the techniques. For developing the techniques, you need much finer resolution than you do once you understand the mechanism. Then you may be able to go back to coarser resolution.

SPEAKER: That's true.

MS. HERING: So, I'm just going to leave it as variable. Once we get to here you're going to be here anyway. Okay. Let's go back to Pete's list. So, we have, I think what we see here in terms of the nitrate is the filter methods, comparisons have been done in the past and probably needs to be done again. We've got where size result data are needed, as collected by impactors again, part of the comparison, but preferably because I would say because of the cost of the measurement it would be done where it was also coupled into a study where the data were needed, such as in a source resolution study.

SPEAKER: And the comparisons

need to be done in different places in the country, because you may get different answers for the same comparison test.

MS. HERING: Yeah, we already...

SPEAKER: Which we need to reiterate.

MS. HERING: Reiterate, okay. And the revolving real time methods, if they're going to be used for long term monitoring and run against the filter based method.

SPEAKER: Pete in his presentation this morning gave us a whole list of things that require evaluation.

MS. HERING: Yes.

SPEAKER: Can't we just deal with that list? We don't have to reinvent the wheel right now, we did it already.

SPEAKER: Well, we're looking forward here. I'm not sure that this necessarily contradicts anything I talked about this morning.

MS. HERING: Well, I have a different list. This was...

SPEAKER: What I'm kind of thinking is that if we can set some targets that we think are achievable and possibly important, I think that is a well known, there's a report put together by a committee chaired by John Seinfeld back in the mid '80's, maybe

the early ‘80's, which pointed out the importance of measuring hydroxyl and millions of money was spent on that. Eventually it was successful and of course that has really played an important role in our understanding of atmospheric chemistry. So, I’m wondering if we couldn’t put, if we couldn’t agree that perhaps there are some very important goals, maybe not just in individual species, but maybe some broader goals that we should try to highlight and endorse as a community.

MS. HERING: I mean that’s one reason I started off with sort of general things. I wanted to see what, in terms of general ideas, that people came up with. But I think the nitty gritty issues, I kind of wanted to get back to the organics issues, because this is one of those big issues that we had raised and we had some specific ideas there. Is it possible to open the door? Too loud, you can’t hear? Okay. I’m about ready to wilt. Okay.

We talked about...okay. Well, you can go ahead and close it. We talked about issues with regard to organics characterization and with regard to the partition gas particle, partitioning, how that relates to sampling issues. We talked about possible analysis methods for looking at categories or classes of organic compounds. We talked about archiving samples from coarse filters for analysis by multiple methods at

different labs, to see the analysis compared. We haven't talked, we didn't really talk about sampling issues, except that there is collection of impactors versus filters, various types of neuters, concentrators have been proposed.

SPEAKER: And these are all related to the source receptor relationship, at least the list that I'm looking at.

MS. HERING: They're also related, I would say the health community is one of the 10 organics and it seems whatever is in there, it's one of the 10 target items.

SPEAKER: They've identified some. HEI for instance is currently undertaking a major exposure study on carbonyls and specific carbonyls and the measurement problem with carbonyls is fairly severe. Certainly carbonyls should be included on the list.

MS. HERING: I think that goes back here.

SPEAKER: Are they on there already?

MS. HERING: Carbon class, you want carbonyls specifically. We'll just add it.

SPEAKER: I think there are other health studies that are using, looking at organics and particles.

MS. HERING: Peroxides is one we haven't gotten too yet.

SPEAKER: I think it's the organic peroxides that are...

MS. HERING: Organic peroxides, okay.

SPEAKER: Certainly that is one too, because that identifies things from a health point of view. There's a whole bunch of other compounds identified in that report.

MS. HERING: Yes, it's referenced.

SPEAKER: I'm saying that.

MS. HERING: Okay. And I think this fits, I think in terms of species, assessing the status, I think we've sort of assessed the need here for these things. This sort of falls into your category, your tables rather nicely. In some cases we've identified possible, not for the organics, we haven't really identified possible real time methods for the organics characterization.

SPEAKER: Well, there is work being done on mass spectrometry in real time. It's got a long ways to go, but it does offer possibilities.

MS. HERING: Yeah, I do have it. Okay. There's also FTIR possibilities there. A lot of sampling issues.

SPEAKER: Did I miss something?

Are we going to identify carbon?

MS. HERING: Oh, as an OCEC?

SPEAKER: Yeah.

MS. HERING: I had sort of glossed over that.

SPEAKER: I think it's kind of late. I don't want to...why don't we just, OCEC.

SPEAKER: It's in the Turben Report and you should minimally look at TOC, total organic carbon.

MS. HERING: We know this is going to be done, we know it has similar issues, on this table it's going to fit like the nitrate. Except there are additional analysis questions, laboratory analysis questions. But otherwise that's fairly simple.

SPEAKER: I think the more general is TC, total carbonaceous material. Whether or not it's worthwhile splitting it out is to be thought about.

MS. HERING: Do you mean, by total do you mean total particulate carbon material?

SPEAKER: Total particulate carbon, total carbonation material.

MS. HERING: In the particle phase?

SPEAKER: Particle and gas phase.

MS. HERING: See, that's what I was trying to get at, you mean both.

SPEAKER: Yes, absolutely. But if

you just think about the TCP, the particle phase, then if you, then you have to have that as well. You have to have both. TCP as well TC too.

MS. HERING: Okay.

SPEAKER: An important question there is the amount of oxygen, hydrogen, etc. associated with that product.

SPEAKER: Yes, and then of the compounds that we identify what fraction of the total they represent.

SPEAKER: Yes.

MS. HERING: See once you start getting to this you start getting to organic speciation I think.

SPEAKER: Yes.

SPEAKER: You need to have this in order to have the speciation in perspective. How much of the stuff you actually account for.

MS. HERING: Yes.

SPEAKER: For instance many of the chemists are really great for looking for recyclers, but there are only 1,000 or one ten thousand of the total carbonaceous mass that we don't.

MS. HERING: Before we get off the list and right to what we've talked about here, off the list of species, one thing we haven't talked about is elemental carbon or black carbon. Other than filter

methods, there's epilometer methods...

SPEAKER: That measures absorption. You have to be very careful.

SPEAKER: And they're not equivalent.

SPEAKER: It's fine to measure absorption and whether you translate it to black carbon or whatever isn't real meaningful. But absorption and scattering and extinction are continuous measures.

SPEAKER: And there's some real time.

SPEAKER: You lose measurement of particulate materials suspended in the atmosphere at the point of sampling, which was brought out in one of the other workshops just now about time resolution. You can't get high time resolution for everything. You could associate those things that give you high time resolution, you can associate with higher, with more integrated sampling and see whether there's a correlation or not and say something about things. You don't have the capability for measuring.

MS. HERING: Actually what I want to move onto just falls on that exactly, which is a physical measurement of the aerosols, which we haven't really talked about very much, except in the context where these measurements for aerosol, total aerosol mass and I think there's some very interesting questions here.

We have a half an hour, so what I'd like to do is take about 10 to 15 minutes on some of these physical measurements, which absorption is one and then see if we can come to some sort of closure.

SPEAKER: Also tomorrow morning.

MS. HERING: Oh, we also have tomorrow morning. It seems like an awful lot to try and do. And then there's biologicals, which we haven't talked about at all and peroxide is on this list. Is that important for health? It's not on the health guides.

SPEAKER: The health people also mentioned the list that Marley put up, in metals they talk about compound rather than the other ones.

MS. HERING: Okay, physical measurements, physical characterizations. Number, surface, I'm going to put down size distribution, although you can always, for which you often get volume. Five nanometers to 10 microns.

SPEAKER: Three.

MS. HERING: Three nanometers to five microns. We've got water, particle bound water. I don't know if you want to, it's usually measured by physical means.

SPEAKER: Density, particle density.

SPEAKER: I think it would be helpful to separate properties from measurements of integral properties of distributions. So, things like particle

bound water, density, index and so on, are sort of different categories.

MS. HERING: There you go. Scattering needs to be up here.

SPEAKER: Extension.

MS. HERING: Some of these relate to secondary standards, rather than primary standards. In other words, visibility. There's been very strong emphasis on how we shouldn't ignore the secondary standards, because they are what the public sees more than anything else. There's questions. I mean here, questions, is there a need to compare size distribution measurement methods? Is there a need to improve these methods? Make them more generally useable?

SPEAKER: With respect to a need for evaluation?

MS. HERING: Uh-huh. (Indicating affirmatively.)

SPEAKER: We really have problem sites with those three, trying to get them to match.

MS. HERING: So, there's some...

SPEAKER: Most of the instruments used for making those measurements, except for distinction.

MS. HERING: Call this A, the status of A is there are conflicts among measurements, you're saying?

SPEAKER: Very hard to get them to add together in many cases and in other cases they go together wonderfully.

MS. HERING: Sometimes.

SPEAKER: But you never know in advance.

SPEAKER: All of those measurements above the line, I absolutely agree that there's refinement that can be done to improve the ability to quantitatively make measurements and resolve measurements and so on. But I think it's fair to say that our first order is to make those measurements in pretty good order, pretty good hands. It's not like the problems that we're dealing with for organic carbon or volitalization, semi volatile carbons. These are a different order of problems. We're always going to be trying to improve them. We will continue to try to improve these things. But it's, we really have this much better in hand, than we do some of the other measurements.

MS. HERING: I think my sense on these measurements is more their usability. Another, this is perhaps a topic for tomorrow, but on the list there's also, we won't, we talked about ambient measurements and everything we've talked about today has been in the context of ambient measurements. A charge that was also given to the group was also

looking personal exposure measurements and this means appropriateness for doing certain measurements, appropriateness for doing measurements in indoor environments. I don't know if that's completely out of the charge of this group or not.

SPEAKER: Well, when you separate those two, are we talking about indoor measurements or personal exposure measurements?

MS. HERING: They're different and, I mean presumably from a science point of view you need to do all three. I think there are questions about some of these measurements. There are questions about refining your environments or even are any of them appropriate for personal measurements. So, moving on...

We talked about archiving data, as data is collected at the super sites, and actually at particle characterization networks throughout the country, thinking about data format for archiving. This is an easy one for this. It's an important issue that needs to be addressed up front, some of the solutions, examples that were given, that are possible, examples that were listed as possible starting points and I think it's...

SPEAKER: EPA/NARSTO was part of that and NARSTO has already got an archive, data management and archiving system set up and two documents prepared that provide guidance.

MS. HERING: This is the one that was referenced, the NARSTO.

SPEAKER: But I guess that's the generic thing that's been set up. The specific, actually working form of it is whether or not, which now at this point emulates.

SPEAKER: There may also be some databases related to climate program.

MS. HERING: The reason we're bringing up the format for reporting particle data is that it's a lot more complicated than reporting ozone or carbon monoxide or NOX data.

SPEAKER: The overall manager for the NARSTO data is Oakridge and I believe they're the same people who are managing climate data.

SPEAKER: I believe that's correct and the actual location, the big computers for this stuff I think, which are NASA supported.

MS. HERING: Then in a general way, just talking in a number of different ways the issue was brought up of calibration standards, development of standards. I think especially as you move into looking at more on-line measurement methods for particles, how you calibrate those instruments is going to be an extremely important question. It's been mentioned by many of you here and as well as #10 and the one that's #20, these numbers are a little bit random. But I think

the issues of standards and perhaps that's something we can come back and visit a little bit again tomorrow.

SPEAKER: It's the more difficult one, really crucial.

MS. HERING: I mean it's one thing to have IC standards for laboratory methods, it's another thing to have standards for chemical speciation in the field and sizing in the field. So, this relates to chemistry and physical measurements.

SPEAKER: A question from this morning, indicated how one might determine accuracy. The only item that was left out of the list was comparison derivation. Get information about...you can take the observations from it and you construct what might fit at the time of sampling. I don't know if you intended to include that or not.

SPEAKER: Well, to a certain extent, in some cases it's implicit, in other cases it's not achievable. So, it really depends very much on the measurement.

MS. HERING: The other thing we talked about was comparisons to a regulatory standard versus comparisons to the best estimate of reconstructing it, as you will, what's in the actual estimate of the aerosol. This is, so when you talk about calibrations there's even the question of what goal that we're after and they're two different things that have to

be recognized. That's another point that, just summarizing a point that is on one of these flip charts somewhere. Is there any other, I don't know, we talked about for...so, this is for tomorrow and I think also...I'd like to know what number I'm on now.

SPEAKER: Six.

MS. HERING: I'm on six? Four, actually it says, I saw this...five, six, and then we talked about or we will talk about tomorrow, there's this whole category of biologicals and it was one thing that was mentioned. It's in number six over there is looking at testing biological mechanisms, mechanistic endpoints for interactions of particles with, I don't understand this field, somebody help me.

SPEAKER: Well, two different things. With #6 what I was suggesting is that if you have a biological course, then you figure out a way to actually test that in the field along side your sites. But for this one I think what you're talking about is biological particles, micro organisms and toxins, biological material or biologically derived material in the air, such as bacteria, fungi, viruses and that type associated with those.

MS. HERING: Then there's, we haven't discussed the measurement issues associated with that. I'm clueless myself.

SPEAKER: There are many reviews

on measurement methods and biologicals available. They also use those. So, take your pick. There's everything.

MS. HERING: Time has flown by. I want to thank you for your time. What I will try and do, we can meet again tomorrow. I'm going to try to put together a list on the number one item here for our chemical and physical characteristics of particle standards, current questions and what are some things that might be done. We can, so you can just maybe make some handwritten corrections on that tomorrow. We might look at taking a crack at putting some priorities on those things tomorrow and then look at the, spend some time talking about calibration standards. That's going to be a real big issue. If there's people here...the whole question of evaluating accuracy. Then there's the other one that we haven't talked on and that's going to require somebody other than myself leading that discussion I think, is having to do with the airborne biological materials, gas phase. Let me add that. Okay. Well, it's not necessarily nine, but gas phase, I'll call it semi volatiles.

SPEAKER: Then there's still questions about measurement too.

MS. HERING: That's not the purview of this committee, don't have to discuss that one. So, thank you very much.

(**WHEREUPON**, the Breakout Group Session was concluded at 5:08 p.m.)

C A P T I O N

The Breakout Group Session in the matter, on the date, and at the time and place set out on the title page hereof.

It was requested that the Breakout be taken by

the reporter and that same be reduced to typewritten form.

EPA/NARSTO PM MEASUREMENT RESEARCH WORKSHOP

"Breakout Group; PM Measurement Methods"

July 23, 1998

MS. HERING: Our job this morning, we have an hour, I guess an hour and a half or maybe, I don't know when they're going to give us a break, so maybe try and finish in an hour and a quarter. Again, somewhere I believe we have a court reporter so that when you make your comments they ask that you give your name, so I'm Susanne Hering, and what I did last night was to take our flip charts and combined them with Wes's very thorough notes and I tried to put what we talked about yesterday on, in an organized fashion rather than the sort of James Joyce fashion in which we put all this material, our ideas out in a rather organized way, and so I want some comments on how I did this, especially for having, doing it at midnight, who knows how accurate I was.

So I put together, first of all here I saw as what people seem to indicate the objectives doing measurement methods, comparisons, and evaluations of the supersites. It seems to me that there were three things that were mentioned here. One was providing comparison among the methods that were going to be used at multiple sites over a period of a few, of the immediate three years until, that we know that the sites

are going to be running. For instance, an example being the speciation monitors, and then to provide a platform for field comparisons for new emerging methods, and the third item that I'm listing here under objectives because it seemed to be so important from the point of view of those of you who were in the workshop, and that was the point of evaluating methods for calibrations and standards. That's something, that's a point I'd like to come back to and to fill in some details today.

We talked about accuracy, whether or not we were going to be comparing against the standard or assessing how representative a measurement is of what's actually in the air, and pointing out that these are two different questions. I don't know where I should stand, because if I stand over here I can't see. Then, and these are, these sorts of questions can be defined as part of the data quality objectives. Data archiving was brought up as an important sort of up front kind of issue that needs to be dealt with up front, not afterwards and here's an example of NARSTO formatting questions for particle data. Disseminating results for more routine measurements as in, such as the chemical speciation results, monitors, disseminating results. I mean by this not just so much the measurements, but the results of comparison testing, and so there could be some guidance as we move along on whether they're

good techniques.

Okay, and then we went through and we examined measurement issues for specific pollutants. We went through the list of ten. We went through measurements and physical characteristics of particles. We talked about size and total chemistry measurements because that was explicitly listed in the Source Resolution Section. What we didn't talk about, but we might want to come back to today, is measurement evaluations that would be useful for people doing indoor measurements for personal exposures, is something we didn't talk about. We talked about time resolution, and this is something that input from the other groups would be useful with regard to, but we pretty much came down to longer ones are okay, but almost the shorter the better. Suggestions as short as ten minutes for source receptor modeling for secondary pollutants. Longer periods being okay for some source receptor modeling.

We discussed the status, status needs of possible approaches for measuring these parameters, and for some of the parameters such as organics or transition metal analysis, we really just looked at analytical needs. We didn't talk about automation. That doesn't seem to be there yet, but for other things such as doing sulfate or nitrate. We talked, or physical size distributions are already there. We talked about

approaches for automated high time resolution measurement. Please, if you think I'm doing something, this is not a correct summary, please pipe up, because you're going to...

MR. WHITE: Can I interrupt for just one moment? I left the session early yesterday afternoon. The room was just so hot I just couldn't take it. You said that we discussed sample storage. I had asked a question about sample storage, and by the time I had left the room, I didn't have a clear answer. Did you answer that question after I left?

MS. HERING: No, I don't think so.

MR. WHITE: Ah, okay. We don't know how we're going to store samples. Is that it, or everyone's going to do it however they think best?

MS. HERING: Well, I mean, there's, we didn't really discuss it.

MR. WHITE: Okay. I'm sorry for interrupting.

MS. HERING: It's on a list of things.

MR. ONDOV: Well, at this level, that's probably what you need though.

MS. HERING: Pardon?

MR. ONDOV: At this level, that's probably what you need. You need the details of protocols.

MS. HERING: That's not what we're

after. That's on my draft, and I don't think it made it on my list here, so we can figure out where to stick it on, okay, so we'll have to hand write it. Field comparisons, when we're doing field comparisons among methods, this is perhaps, these are things that we mentioned about, we discussed that a field comparison shouldn't be just, well, we'll just throw these instruments together at one site. It should be a well planned, I said analytical approach for, so that you can do enough measurements, or you do your comparison measurements in a way so that you can understand the reasons for differences, not just to assess what those differences are. We would include the emerging automated methods together with the traditional filter based methods, because that's an optimal use of resources, testing individual aspects of the measurements, consider and compare inlet differences, include co-located measurements of the same type. Measurements should be at multiple sites, but not necessarily at the same time, and we should plan that these intensive periods of methods of comparison to be coordinated with other intensive studies so there's better use of the data. People didn't want things to be driven by the FRM.

MR. CHING: Can we go back to that very last point there? You have it under field comparisons among methods is intensive studies. I

think maybe just an emphasis on the fact that you can make your intensive studies build around, intensive studies not just simply for field comparison among methods, but as an integral component of the experiment.

MS. HERING: Rather than just coordinated, it'd be an integral part.

MR. CHING: In addition to method comparison, become part of an integral study.

MS. HERING: Yes, that's...your concern is the way I worded it. Is that right?

MR. CHING: Separate wording.

MS. HERING: Pardon.

MR. CHING: Should be integral.

MS. HERING: Okay. I say it should be at the same time, but it should be an integral part of it is what you're saying.

SPEAKER: I know it's hard, but why shouldn't we have quality assurance?

MS. HERING: Yeah, okay. With regard to the Federal Reference Method, it was agreed that at least when comparing the, with measurements that measure some indication in mass or the chemistry to run the FRM at the same time, but not to be driven by what the mass value is from that sampler, but rather to assess how that measurement relates to what our best estimate is of what's actually in the air. So it's more

assessing biases. Yes.

MR. ONDOV: Again it may be out of sequence here, but did you all discuss any neurological measurements in the context of your discussions yesterday?

MS. HERING: Not methods.

MR. ONDOV: Or at least needs. Somebody mentioned it the other day at some point, but I really think if at these supersites they can have remote sensors for the temperature structure, that would really help a lot in interpreting concentration data. So that we get conversion highs and things, because typically we go out and the only place we can get it is twice a day at the airport which has nothing to do with the middle of the city where we're making measurements. Especially in the Chesapeake Bay region, you know.

MS. HERING: Oh, yeah. Interpreting it with regard to understanding sources.

MR. ONDOV: Yeah, sources, mm-hmm.

MS. HERING: But not necessarily with regard to understanding how methods compare.

MR. ONDOV: Probably not.

MS. HERING: But maybe.

SPEAKER: Will you have other bullets to show us on your summary?

MS. HERING: Oh, yeah I've got this whole stack.

SPEAKER: It may be in there.

MS. HERING: Yeah, I didn't, I don't know where to stick it, but I mean, it should be, certainly if it's part, an integral part of other intensive studies, there will be other measurements. I mean, I can't imagine that someone would, should I...

MR. ONDOV: Oh, I can imagine that there's a lot of things...

MS. HERING: Okay, okay, integral part, okay..

MR. ONDOV: Why don't you pull that last bullet up above down so the bullet...

MS. HERING: Concurrent, so...

MR. ONDOV: You write it down, and then other groups write it down, and then it'll have more weight than if nobody writes it down.

MS. HERING: So we need Meth and..

MR. ONDOV: I'm thinking, you know, if they can get this feasible, reasonable cost to do remote sounding for something like temperature structure, and as far as I'm considered, they should have a 3-D ana-monitor or something that you could make terminate measurements.

MS. HERING: I'll have to say always.

MR. ONDOV: We want to interpret

the data, we want to know what's going on in the atmosphere, right? I mean we want temperature, and we want to be able to interpret that.

MS. HERING: Any other critical things, besides Meth, I mean...

MR. ONDOV: Well, I mean, I'd measure the whole solar insulation, and Jason can tell you...

MS. HERING: Solar radiation doesn't usually...

MR. ONDOV: To the typical air pollution chemist it means wind direction, wind speed, relative temperature and relative humidity and that's it. Then you want to figure out, well, gee where was the mixing height, blah, blah, blah. You have no clue.

SPEAKER: But actually, they're getting that from the radar...

MR. ONDOV: Well, I still think it should be on the list.

MS. HERING: Well, we'll just put it on the list. It doesn't hurt it. Solar radiation, gas chemistry, right.

SPEAKER: Should relate to air mass characterization.

MS. HERING: Pardon.

SPEAKER: Absolutely.

MS. HERING: Okay, let's see. We've

got, oh this is just very quickly what I put together on organics. Just sort of going through the individual ones. Statuses, we can only identify, this is in terms of saying what's in the organic fraction. All right, that we can only identify a fraction of the organic compounds. The list is very long. Sampling is difficult. There are sampling issues. This is quite complete. We add recommendations, had to do with examining new methods, new analysis methods, for species classification of carbon compounds. Carboniles, I don't know whether we need a new method or not, but carboniles was mentioned as an important compound. Compound classes, dividing polar and non-polar classes of organics. Reference was given to Mark Trupin in an EPRI report. We talked about archiving samples, this is a little bit with regard to your reference material for multiple, for testing by multiple methods or in various laboratories. We looked at comparing impactor versus filter collection, looking at approaches with denuders or concentrators and comparing with aerosol and mass spectrometry data.

MR. ZIKA: Yesterday I spent the day over in health, with the health group trying to have some impact. I don't know if I did or not, but one of the things that was obvious was that they really can't deal in their epidemiological model with detail. They want gross values. For instance, this is the size of a

particle, this is the particle counts, and these are some of their priorities that they've set up. I talked to them about the possibility of using, I'm doing general class studies. For instance, PAHs are potentially a deleterious compound, a class of compounds. There is more than one PAH that does this, and you can measure PAHs rapidly and very, fairly cheaply because everybody has certain properties, and you like to measure them as a group. Biologicals are all going to contain amino acids. Do amino acids as a general category, don't do specifics. It creates, it improves their capability for doing a whole variety of measurements with different groups, characterizing a sample more completely without spending a great deal of resources and money to do it, and so, development of that kind of technology, where you can do a broad class of classifications I think would be very useful to them. Maybe not to us, but to them.

MS. HERING: Yes, and that's something that would perhaps make it possible to get more of such data.

MR. ZIKA: Because very often you do this in a high, fairly high frequency, and you do it that way.

MR. WHITE: Will we expect amino, individual amino acids to be present, or are we expecting proteins to be present?

MR. ZIKA: We expect proteins to be present, but have actually done amino acid analysis, and a lot of what's there is free amino acids. We're not sure why, but seems to be the case.

MR. WHITE: You're not suggesting that we digest the sample and break the proteins down into individual amino acids

MR. ZIKA: Well, that would be the easiest way to do it. Just do a bulk amino acid analysis.

The problem you get into with all detailed analysis is somebody has to sit down and validate all of the individual components, and that's what gets to be expensive. You just group them together as classes, I mean, they can't use that data now any ways because they don't know what they're looking for.

MR. WHITE: Right.

MR. ZIKA: So the question is are there metals, an increase in metals? Are there increases in biological components? Is there an increase in anthropogenic, dangerous anthropogenic compounds like PAHs. Maybe that, that would be more helpful to them at this point. I mean, if they could get some sort of clue as to what group of compounds, or what, where the problem spots are. Then they can go into detail and look for, in the cases of metals, of oxidation stages, specific kinds of metals.

MS. HERING: So these compound classes, you would put a star on here, as especially important, these being examples.

MR. ZIKA: Well, this is, you know, this is a couple examples, but coming up with some sort of categorization of compounds that you can, that could tell you a great deal about the general composition of particles and different size classes would be very helpful.

MS. HERING: Size resolved. How much size resolution are you talking about, just below two and a half or...

MR. ZIKA: I'm sorry?

MS. HERING: How much size resolution are you talking about?

MR. ZIKA: Well, you're talking about the ultra-fines, and then there was an argument about the fact that there's no evidence that ultra-fines are important, and so I don't know where that stands really.

MS. HERING: Okay.

MR. ZIKA: But they were interested, very interested in size classes, and they felt that the PM2.5 and 10 were sort of artificial and, you know, let's look at chunks versus the fine, that sort of thing.

MS. HERING: Okay, well, let's, the next slide has to do with size resolution, so...

MR. ZIKA: Bob's even mentioned another class of compound, pesticides.

MR. STEVENS: They're almost in every sample.

MR. WHITE: What are the major pesticides that you see? I'm sure it varies from region to region, but where you're sampling, what do you see?

MR. STEVENS: Well, in Florida you see the thiophosphates, you see chlordane. In Texas, I mean, there's a whole list. I could send you a list of them.

MS. HERING: No.

MR. STEVENS: Our work in the Brownsville study, we did a survey on pesticides throughout the United States, and I can send you that list of compounds that we see all the time.

MS. HERING: All right. Let's, if we could move on. That's a little more detail than we have time for this morning. Size resolved chemistry, this is something that was in the list of desired measurements in the Source Receptor Group, and this is, we mentioned that this has been done by impactors and by microscopy. It's generally been limited by the cost of doing the measurement, but the feeling was that there were new methods, or even more automation of existing methods coming on-line that offered some encouraging possibilities for getting this kind of, these kinds of

measurements more often and more cost effectively.

MR. ONDOV: There's one thing I just threw in as a sub-note about the comparison between filter or impactor methods and the time applied mass spec. One method could leave you with a sample that could be analyzed later, whereas the other is destructive. So we consider destructive verus non-destructive methods in your strategy for collecting samples. For example, electron microscopy is non-destructive, whereas mass spec is destructive.

MS. HERING: Well, it's, yeah. Mass spec is completely destructive. Usually the on-line, almost all of the on-line methods of measurements are completely destructive.

MR. ONDOV: It's good that it's destructive. It also destroys your budget.

MS. HERING: I think that's more of an issue with regard to sample archiving and reference materials. Is that what you're, we can, we'll get to that. I think, we'll bring that up in a couple more slides again, okay. Physical characteristics of particles, number, surface area, size distribution, scattering absorption, extinction. Basically, I would say in terms of status, most of these measurements already have good time resolution.

MR. ONDOV: Question. With regard to surface distribution, is anybody really doing the real

surface area measurements?

MS. HERING: Well, the epi piniometer, pretty close.

MR. ONDOV: Is that right? Is that what that word meant? I thought it was a religious term or something. I mean the soot surface area means we just take the square of the particle diameter...

MS. HERING: It's a different answer, yeah.

MR. ONDOV: Well, the epi piniometer would not measure the, accurately the surface area of irregularly shaped particles. Because I think if we just take the, well, yeah, because, I mean, simple task is something like, you know, four or five meters squared to gram, and the rest you...

SPEAKER: He wanted a BET surface area measurement. That's pretty standard, and maybe even a mercury probe...

MR. ONDOV: It's standard, but it's hard to do unless you got a bottle of stuff.

MS. HERING: Yes, exactly. Having done it myself in my old days, it takes a fair amount of material to do it.

SPEAKER: But I think I would look, I would note that as, you know, as sort of a flag that maybe that's something somebody clever could zoom in on.

SPEAKER: Yeah, a research area.

MS. HERING: Yeah, because I came up here with, what happened to my recommendations, it's blank, okay. So let's, improved, always need better methods, right. Especially surface area.

MR. ONDOV: Well, I mean, if any of these hypotheses about surface area are going to be, you know, borne out, that could be an important measurement. It may turn out that it's not, but...

SPEAKER: Well, and, you know, it's a question of whether you want total surface area including the surfaces of internal pores or whether you're really interested in the surface that you come into contact...

MR. ONDOV: But if you don't, if you can't measure both, then maybe you don't know.

MS. HERING: So there's improved methods, better insight into individual particle morphologies and so forth is...

MR. CHING: So then in a case of a surface area, the water bound or the aerosol water will play a major role in terms of the whole surface area, because that swelling to moisture is going to....

MS. HERING: So there are many science questions here.

MR. CHING: So we've got a real question of interpretation..

MR. ONDOV: Well, soot collapses, right?

MR. CHING: Well, it does, you know, in terms of the measurements and the history of the sample and then relating it to health or whatever. I think we have a major problem of interpreting aerosol water in the measurement. It's so dynamic, it's over the course of a day, 24 hours, we have great changes in a particular particle. So I don't know how to handle that, but that's really critical. We've been worried about that for years. We need water.

MS. HERING: Water. I didn't actually put, I think, did I miss. I think I got, you know, there was a limit to how much I got down, and I think I don't have particle, what happened to my particle bound water?

MR. CHING: Water bound aerosols and then determine, interpret that information from that method.

MS. HERING: There's many research questions. There's the...

MR. CHING: Peter can, I mean, Peter's the expert. The expert's here on that subject.

MS. HERING: Oh, yeah.

MR. McMURRY: Well, I think with respect to water, probably to answer the kinds of questions that you need, you need experimentally

verified models, and if you have a model that you believe in, then you can exercise that model to calculate how much water is present when, as a particle flows into the lung for example when the humidity changes. I believe that's the way to go.

MR. CHING: But it is the ambient concentration that tells if the model that we have would be so dynamic in terms of aerosol water.

MR. McMURRY: I think in principle you can handle that.

MR. CHING: We would be able to with our methods?

MR. McMURRY: I think there's, I think that by developing models that you compare against experiments, you can do that, and a fair amount in that direction has been done already.

MR. CHING: Would that be something like cooperate with a supersite?

MR. McMURRY: Well, yeah, as you were talking it occurred to me that we have focused narrowly on measurements, which was our charge, but I don't know who in this community has been looking at models to answer questions like that, and that certainly is an important part of the whole thing.

MS. HERING: I'm going to say coupled with models here.

SPEAKER: What about...

MR. McMURRY: Well, he hasn't looked at aerosol models so much as he has looked at I think as mechanistic models for production of secondary species and relating sources of primaries and reactive gases to what is produced, which is important to mention, but it doesn't deal with the physical chemical properties and their importance.

MS. HERING: So, I mean, if we were to, if we were to extract some larger sort of recommendation here that at these supersites where you have intensive measurements, there are specific research questions that can, that it would benefit to be answered there. Perhaps special experiments with ambient aerosols that are coupled with modeling work to answer some of these questions about particle bound water being one that's brought up here, about actual particle surface area being another one.

MR. McMURRY: About the properties of the organic compounds that are in the particles, their volatility, their hygroscopicity, that sort of thing. Yeah.

MS. HERING: So, let me put that one, where's my organic slide? Organic, so we're recommending under the organics as well, sort of special focused research experiments

SPEAKER: Sort of talk about artifacts, both positive and negative artifacts.

MS. HERING: Yeah, and also just getting beyond the measurement issues, and characterizing these particles. It's, we'll put, artifacts, okay.

MR. ZIKA: I think it's of critical importance with respect to that last point, is the hygroscopicity or the hydrocollicity of the particles which is going to be largely determined by the surface characteristics because remember when they arrive at tissue they're going to encounter surfactants, so their behavior is going to be greatly modified by what their surface characteristics are, I think, when they, when they contact tissue.

SPEAKER: I want to comment on that about that it may not be an equilibrium problem either. It could be a rate limiting thing, that if the surface inhibits the transfer of water. You might have it, not necessarily, decrease the amount of water that is taken up by the particle, but it decreases the rate that you would have water incorporated.

MR. STEVENS: There's some interesting work being done by Jane Gallagher. She's going, she's having, taking air samples but at the same time she's going into the lungs of volunteers, taking particles out of lungs and then examining them by scanning electron microscopy to relate the ambient exposure to what the individual is, and I would say

that's what I call exposure carried to weight, its logical limit. It turns out there's a lot of people who wanted to volunteer, and they're able to allow that procedure to go on, and she has a wonderful paper coming out on how to do that process, and it's part of EPAs exposure program and SEM program, it's an extremely important part.

MR. ONDOV: There a corollary to that too, by the way, it's the nasal lavages.

MR. STEVENS: She does that too. She does all three.

MR. ONDOV: Snot from kids' studies.

MS. HERING: Okay, I want to, just to move on here. We have, we talked about...this slide I think I'd just as soon kind of skip over fairly quickly. We talked about mass and mass surrogates, we listed methods, same for inorganic ions, traditional OCEC measurements, and these discussions all had sort of a similar theme in that we do need despite even for inorganic ions that there are methods that have been established in certain locations as giving comparable answers among very different methods, that it's still going to be worthwhile to run these methods side by side and at the same time to include the more automated methods so that we can do these comparisons all at once. We promised to, Paul Soloman here wanted us to talk about gases that interact with

particles which is ammonia and nitric acid, so I put it on the list for today. So we, I don't know if we, we were listing measurement methods. I mean there are, of course, filter, denuded filter methods, or denuder methods, right?

SPEAKER: Right.

MS. HERING: We have denuder methods. There are some real time methods for these species, right.

MR. STEVENS: The wet, the wet denuder is one. It's real time.

MS. HERING: Yeah, we've got...

MR. STEVENS: There's hemi-luminescent methods.

MS. MIDDLEBROOK: Yeah, there's chemical ionization methods.

MR. STEVENS: As a difference measure of course.

MS. HERING: Yeah, I think we got NOI difference up here under inorganic ions so it's a little, and wet denuder.

MR. STEVENS: There's a differential optical off sulfur spectrometer, DOAS.

MS. HERING: Well, maybe it's the TDLA.

MR. STEVENS: No, it's different. DOAS.

MS. HERING: No, they'll ask if it's TDLAS. There's a whole list of these. Some real time.

MR. STEVENS: I mean, it's, in the Netherlands it's one of the instruments that they use to modify load.

MS. HERING: But there's a whole host of these, these methods, and then, pardon.

MS. MIDDLEBROOK: Chemical ionization mass spec.

MS. HERING: Chemical mass spec, okay. I think the main point is that, that these constituents be included when we're looking at measurement methods.

SPEAKER: What about the VOCs and some ideas?

MS. HERING: That's under organics or do you want...

SPEAKER: It should be included here.

MS. HERING: Should be included. Oh yes, of course. Of course.

MR. ONDOV: Somebody should write on this list of things, not only should we make all these measurements but then somebody should actually look at the data and that should be built into the experiment. That's not a joke, really.

MS. HERING: No, we need to put

that, that's something that needs to be added on one of those initial slides.

MR. ONDOV: Nobody's looked at the data from the Baltimore site for two years now, as far as I know.

SPEAKER: Well, that's right.

MR. ONDOV: And it takes a little funding.

MS. HERING: Okay. Should we call it concurrent data analysis on this main opening slide here?

MR. ONDOV: I think the data interpretation, data analysis, protocol plan, or something should be...

MS. HERING: Concurrently, concurrently planned?

MR. ONDOV: Yeah, it should be integrally planned with the, to follow the data collection in a reasonable manner instead of waiting five years or something.

SPEAKER: I think we can add to that dissemination of the information afterwards, because so much of it stays in reports.

MS. HERING: No, this needs to be really right up here. Well, data analysis compares...

SPEAKER: It's overall. Aren't we talking about data analysis for everything?

MS. HERING: Yeah, it's for, for all, whole, everything, okay. I'll put a big star.

SPEAKER: Right. There's going to be so much data generated in these data bases that's available to everyone.

MS. HERING: Pardon.

SPEAKER: It's called dissemination, in other words applying.

MS. HERING: That's, well, that 's applied a little bit under the archiving, isn't it? Not quite. Data base. Where'd this one go? Okay, data archiving, disseminating results from work,, and data dissemination, right. Data distribution, availability, what do you want to call this? Hey.

SPEAKER: Paul, you're being paged.

MS. HERING: You want to call this data availability, data dissemination.

MR. SOLOMON: Results, after the data analysis are done.

MS. HERING: Yeah, well, we've got disseminating results here.

MR. SOLOMON: Oh, okay. I'm sorry. I didn't see that.

MS. HERING: But I think issues of data availability, data exchange are important ones that have to be addressed, right?

MR. CHING: Well, we have web pages now, so you can download data, instead of people archive this.

SPEAKER: You all were talking about data. I was talking about results.

MR. ONDOV: This idea of the database thing, you know, somebody could do a masterful job if they would disseminate their database accessing program or something like that, so everybody doesn't have to get their own database.

MS. HERING: Okay, the, there is two big topics I wanted to, these are going to be so out of order. Big topics, we talked about, well, metals and peroxide. I just, biologicals are a, something we did not discuss, and the other, I'll give you a choice of order here, and the other issue, and I think it's a big one that I'd like to take some time with this morning is talking about reference materials, calibration issues, because I mean, we don't have, for an ozone monitor there...

MR. STEVENS: Is it a reference photometer?

MS. HERING: There is, there are, yeah, I guess you just generate the ozone and then you have a reference photometer.

MR. STEVENS: Yeah, and then you calibrate your generator, and then the generator

becomes a transfer stable.

MS. HERING: We don't have, for sulfur dioxide you get calibration gases and dilute them down, right?

MR. STEVENS: Certified by NIST.

MS. HERING: For particles, what do we have?

MR. STEVENS: NIST is working on collecting large volumes and the particles that their, St. Louis and Washington's particle standards are gone, so they're embarking on gathering samples for both organic and inorganic. They got a little bit, they got a small program going in this area, but it's basically particles, not other molecules, it's your denser materials, and they're collecting them in Baltimore.

MR. ONDOV: They're collecting them by filter?

MR. STEVENS: They're collecting them by a filter, and then they're going to do a consensus analysis, and then they'll provide them out and provide them to the investigators, for standards.

MS. HERING: So one idea was...

MR. SOLOMON: So that provides the same principle with a filter base...

MR. STEVENS: I'm just telling you what they're doing. I'm not saying it's right.

MR. ONDOV: Actually they do want a

filter based standard, but actually we are collecting the samples for NIST, so I can tell you what we're doing. It's going to be on a filter. We're going to wash it off...

MS. HERING: Quartz filter?

MR. ONDOV: No, Teflon material. We're going to wash it off, okay.

MS. HERING: With what?

MR. ONDOV: With water, then we're going to, and then, because it's, I mean, because we got to get it off, okay. Then we're going to freeze dry it, then we're going to give it to them, and then make it a reference material. They're going to analyze it, they'll probably analyze it, and then they're going to, some or all of it, they're going to resuspend and put down on filter so that the people who are doing x-ray fluorescence will have it as a reference material, a filter based reference material.

MS. HERING: What if it's not water soluble?

SPEAKER: It is water soluble.

MR. ONDOV: Well, it turns out, it turns out that we can remove more than 90 percent of the carbon physically, just mechanically. We are, we are. The Teflon has pretty good release properties.

SPEAKER: Like what, ethanol?

MR. ONDOV: Not ethanol, but...

MR. STEVENS: Well, you got to

remember, what they're trying to do is get something that's more or less representative, the best they could do. The second thing John doesn't know about, they also want to collect a sample for organics.

MR. ONDOV: No, I did know that.

MR. STEVENS: Okay, you did, okay, and they're going to try to collect, okay, you should have, and they're going to try to collect them on special quartz filters so the people can cut a piece out and do this carbon, carbon measurement thing, and the trouble is they have almost no money to do this project, and so EPA or somebody needs to stimulate them as we've done in the past to get them to put these standards out.

MS. HERING: Well, this was, the reference material, the idea of collecting on filters, actually it was proposed yesterday, I believe, to actually do such collections at supersites where you have all these other measurements as well, and so I don't know if it's compatible, but this is a suggestion that was made and raised that it's not something you say, okay we just go out and do it. There are questions about how you do this collection. What material you're using. It's a big issue.

MR. STEVENS: The filter material they're going to try to use is the same federal reference, material that's used with the Teflon filters with the rings.

MS. HERING: But you can't directly analyze that for carbon.

MR. STEVENS: Well, I'm not finished now. This is, this is for trace metals. They will, they will use the best quartz material, lowest blank they can get their hands on, and they're going to do that. Now the problem is, one person is doing it. George Cloud, one individual, and he's got a little bit of money. What should happen is upper management at NIST and EPA should sit down and come up with a plan, and I think that's what you ought to say here.

MS. HERING: Well, I put down NIST, involve NIST.

MR. STEVENS: Well, NIST and EPA, because I don't think NIST, NIST only responds to some clients' needs.

MS. HERING: Okay, so NIST.

MR. STEVENS: EPA.

MR. ONDOV: You need a wide variety of reference materials.

MS. HERING: Yeah, many...

SPEAKER: You need a bottle of stuff besides these filter based..

MR. STEVENS: Yeah, that's the other thing we need, too..

MS. HERING: Many types.

SPEAKER: Spoon it out so you can

do your graphite furnace and blah, blah, blah. Do what you want to do.

MR. STEVENS: You're right. You're exactly right. The way they did this before, they had a huge bag house they took into St. Louis, and they ran it for, I don't know how many months, and then they scraped the stuff off the bag, and did what John said, resuspended it, dried it, of course.

MR. ONDOV: Well, actually they didn't do that.

MR. STEVENS: And then they made bottles of, which they sold for a lot of money to a lot of people.

SPEAKER: You could have fungicide in there too. It's not totally recommended because of the aerosol content is so run up.

MS. HERING: It seems to me that the issues about what types of reference materials are collected and how it's done are big questions that need to be addressed by more than just the person who gets the contract to do it.

MR. ONDOV: It's a research effort.

MS. HERING: So this is a, it's an issue that needs to be examined carefully. Would you agree with that? Maybe...

MR. ONDOV: Absolutely.

MS. HERING: Should we say,

research input onto this?

SPEAKER: That's a big question.

MS. HERING: Carefully addressed, something like that.

MR. ONDOV: Important, carefully addressed.

MS. HERING: By many. Should we say that? What about other calibration issues, beyond reference materials, for calibrating particle systems in the field?

MR. SOLOMON: That's the whole thing of delivering a standard of known concentration.

MS. HERING: I mean, do we have a way of doing this?

MR. McMURRY: We have ways that might work, but it hasn't, they haven't been demonstrated adequately. They've been used primarily for physical...

MS. HERING: Exactly.

MR. McMURRY: ...techniques, and they might well work for chemical techniques. I think they should, but it has to be demonstrated.

MS. HERING: Yes.

MR. McMURRY: The accuracy with which you can deliver a known quantity has to be determined by comparison with hydrozone technique, for example.

MR. SOLOMON: Kim Prather the other day was saying that before they take their measurements out in the field, they're calibrated on a multi-point, single particle composition in the lab, but it's not necessarily something to take out in the field. It's not necessarily something that a lot of people would do.

MR. McMURRY: I think it's probably something that could in principle be taken out to the field, but the methodologies need to be worked out.

MR. ONDOV: How about a regular particle? You know everybody, you have an optical particle count and you take a spherical, monitor those first particles and run it through the air, so on and so forth. I mean you might spray something in a nebulizer. I guess DNAs or something.

MS. HERING: Well, you use those metered dose inhalers. You know they give out, there are all kinds of things.

MR. ONDOV: I mean, it would be nice if there were some sort of irregular mono-dispersed....

MR. McMURRY: No, I don't think so.

MS. HERING: No.

MR. McMURRY: Because you'll never, I mean, if what you really want to do is measure irregular particles, then you have to develop

methodologies that will do it, an optical pump particle counter or....

MR. ONDOV: You're trying to measure, oftentimes, irregular particles with an optical particle counter, because that's what's out there you have to do testing on those.

MR. McMURRY: It depends where the measurements are being made. In the east, it's been found that 90 percent of the particle was there.

MS. HERING: Yeah, but there are, I mean, another, another approach that, you know, Peter's used a lot and many of us have used is taking ambient aerosol and taking a monodispersed or monomobility fraction of it by DMA size selection and using that for calibrating at least the sizing of instruments. There's, that's in comparing counts with composition nucleus counters and so forth for efficiency, so there are approaches, but this again is something that it seems to me that we don't have any answers of how to do it. We're not even going out there and saying, well, we're going to compare these different calibration methods. This is even more in the dark ages it seems to me than some of the organics characterization questions.

MR. ONDOV: You know, I can imagine that this is really going to be important to people who want to measure ultra fine, because every

time, every year or two years, I look at the, this aerosol science and technology, and somebody's decided that it's a different charging function instead of the fuchs charging function for the small particles and blah, blah, blah. Yes, every time you look at data published, it always agrees within the packet for some reason, because why, because they only show the data that's at a standard two tenths of a micron that will agree.

MR. McMURRY: I think an answer is pretty well at hand.

MR. ONDOV: Is that right? If you say so, I'll believe you. I wouldn't be surprised to find it published in another article.

MR. McMURRY: It won't be greatly different.

MS. HERING: From a, there are lots of technical approaches that we've heard, are there any sort of organizational approaches to dealing with this issue as, in terms of how it might be used in a, on a supersite? It's a measurement specific sort of thing.

MR. ONDOV: In the Great Waters program they have a pretty good organizational structure. They had to make a report to Congress so they had somebody at EPA that was working full-time, maybe even more than one person, and that had continuity throughout several years and so on and so forth to see that the different components of the work

stay together, have workshops and meetings, whatever it took to get the data published and so on and so forth. I think that they need a czar or somebody. We need to have, you know, they need to put at least one full-time person to be the captain of this, EPA's oversight on this sort of thing.

MS. HERING: So perhaps having it as a defined task, workshops with a...

MR. ONDOV: Workshops that can be responsible for the final report that integrates all of this stuff, so the responsibility mainly is to get the contractors and the researchers to write it, but at least to ride herd so that it's integrated in some way.

MS. HERING: I mean it might be more than one responsible person because we're talking about a lot of different types of calibration. There's chemistry, there's particle size, there's...

MR. ONDOV: Oh, I was just talking about, oh you meant the calibration, I meant for the whole program, the whole supersite thing. To have a champion, somebody's that...

MS. HERING: No, I mean, were you going to speak to that, as to what the organization is?

MR. WEAVER: I'd rather not.

MS. HERING: You'd rather not, okay. It's not our role to speculate here.

MR. SOLOMON: Can we add to the

second bullet, not only the particles but the gases also. Because everybody knows that it's possible to calibrate gases.

MS. HERING: The problem with calibrating ozone.

MR. SOLOMON: The ozone monitors have an interference with water, for example.

MS. HERING: Yeah, they do.

MR. SOLOMON: So you might calibrate it one Rh and assume that's a good calibration.

MS. HERING: Okay, do this. Shall I just say there are issues for gases?

MR. SOLOMON: Yes.

MS. HERING: I think they're nowhere, well...

MR. SOLOMON: It's not routine to calibrate down to an alpha particle.

MS. HERING: If your interference is, we mentioned low concentrations, reactive species, right.

MR. CROSLEY: On an earlier slide you had intercomparisons, obviously calibration issues should be carefully thought of when you're doing intercomparisons. You have to as best as possible have the calibration...

MS. HERING: Okay.

MR. CROSLEY: ...standards that you could use.

MS. HERING: Include cal standards as appropriate, as possible, maybe, with comparison studies. Okay. Any more comments on calibrations?

MR. ONDOV: At some point, whenever you think is appropriate, can we go back at look at the previous slide with the other compounds to measure?

SPEAKER: Metals and peroxides.

MR. ONDOV: What's that?

SPEAKER: Metals and peroxides.

MR. ONDOV: Yeah.

MS. HERING: Yeah, that's the next, well. There were, I said, no one seemed to have, jump on the biological so I went to the calibration. Are we through with calibration? Everyone is, I mean, we haven't really said what these standards should do, but I think it's, I think probably it's important here just to raise this as a very important question, and an important issue that's going to take a lot of careful thought.

SPEAKER: Throughout all this would you not need some kind of protocol established at the supersites prior to the deployment of that?

MS. HERING: Yeah, that's part of, that's actually, I put it in a context of comparisons, but,

because that was our focus here, but it's on the list already as having a...

SPEAKER: You put a bullet point at QA, it covers a whole host of things?

MS. HERING: Well, what did we say? We said field comparisons should be well planned, analytical approach, written protocols.

MR. SOLOMON: I just wondered if one of the requirements for the success of these was more than just field comparisons. Major things like QA, and that kind of thing might be listed under an overall approach to the supersite.

MS. HERING: I need another slide, okay. Then we'll get, let me not lose that one, okay. See we're trying to be more organized than yesterday. So overall issues, planning. I mean, we can all make this list; protocols, QA, data management, right. This is the standard field list, and then data analysis. There's the, I mean, you don't have a field study by just putting a bunch of measurements together. You need, it all needs to fit into a coherent plan of how these data are to be used.

SPEAKER: We need recording of data, recording and reporting dissemination.

MS. HERING: Okay.

MR. CHING: And I guess you establish all this through data quality objectives.

MS. HERING: Well, I think this is even beyond that, right?

SPEAKER: It's part of QA.

MS. HERING: In other words, a coherent plan that takes you from the beginning all the way through results and reporting, reporting of the, reporting of results, and should we put in here as well, having a clearly, even up here, clearly defined hypothesis for study. I believe that's a, that's a kind of a, okay, we can come back to this one and add more.

MR. CHING: By that you mean the health issues, the source receptor issues...

MS. HERING: Yeah, what are the research questions that can be answered. These are, I mean, this particular session, section is being a measurement methods one, which is sort of cross cutting, it's one of the cross cutting issues. We don't necessarily have specific hypotheses we're to, the charge is to look at how we might bring the tools that are needed of what we, in the areas that we suspect are the questions that need to be, that will be applicable for these, these research hypotheses, but the, it needs to be, overall when you look at the supersites, it's there. This is the last slide.

MR. McMURRY: Well, there would be many hypotheses that we'd have to address to resolve some of these measurement dilemmas that we talked

about, so I mean it's not just that we're...

MS. HERING: Yes, okay. Whether or not, maybe what we should say on resolving measurement dilemmas that would be, I said field comparisons, written protocols. What you want here are specific measurement, measurement issue hypotheses, right? I suppose we should go through, hypothesis. Okay, well, it's completely lost. Metals, peroxides, and biological is the last three. Yes.

MR. ONDOV: I just wanted to throw out maybe another one, pans.

MS. HERING: It's not a particle.

MR. ONDOV: It's on particles. I mean you got peroxides.

MS. HERING: Peroxides.

SPEAKER: Particle bound oxidants.

MR. ONDOV: Particle, for example, I mean, pan's a powerful lachrymator, we're looking for something that's going to irritate pulmonary tissues and so on and so forth. They can irritate...

SPEAKER: Oxidized.

SPEAKER: Nitric acid.

MS. HERING: No.

SPEAKER: No, no. Peroxides are oxidants or irritants.

SPEAKER: Is pan an oxidant though? I mean it's the...

SPEAKER: Yeah, it's not.

SPEAKER: It's not. It's kind of an escalator.

MS. HERING: In summarizing what we had yesterday, we talked about metals in terms of, measuring soluble metals, measuring their oxidation state is, it's sort of an area of research. It's not something that needs to be looked at. It's not even yet quite there for methods comparisons. Peroxides that we kind of glanced, went over quickly, there was some question as to what the health, the exposure or the health community meant by saying peroxides. There was, the implication was that they were looking at particle bound peroxides. There was...

MR. McMURRY: You know, Susanne, it seems to me...

MS. HERING: It seemed too vague for us to address.

MR. McMURRY: That if this group was to set priorities, for example, for some of the measurement question. We probably would not select oxidation state or particle bound peroxides, because this is maybe something that we haven't been, as a community, primarily focused on in the past. It might be that the toxicology group would come back and say this is absolutely the most important thing that should be done, and then we would have to respond to that.

But I think that we need to set some priorities for things that we know to be outstanding questions, which may be issues that they're not so familiar with, like the organics and the volatilization. You know, the things that we just deal with on a regular basis.

MS. HERING: Things that we deal with on a regular basis.

MR. WEAVER: I think one of the things that would be useful in our organization is explain the importance of calibrations in the reference materials and other things because the other groups miss that entirely, and they don't want to put any money into it.

MR. CROSLEY: But also things like this, as you identified, is an area of research. I think that's an important thing to be looking at, too. Obviously the metals are important.

MR. ZIKA: When you put up metals and peroxides, you really opened up a can of worms because the health issues, it is incredibly important as to what oxidation state a metal is in. For instance, if you take chromium or copper, they're very toxic in one oxidation state but not in the other, so it's very dependent upon what oxidation state you're in. The other thing is the association. If you have peroxides, now peroxides you're talking about a particle, probably endo peroxides and hydro peroxides, because you're in

an oxygenated environment, you're almost, any free radical that's formed is going to go to an appropriate peroxy compound. They dissociate or they disproportionate to give you terminal peroxides. So you have a whole scope of different reactivities. If you put peroxides and metals together, they undergo fen type reactions and so you get free radical distributions and changes in the oxidation states, so the covariance of the metals with peroxides are very important to understand. If you have nitrate associated, these free radical reactions, which are going to be more acute in the particulate state than they are in the gas states, we always think about free radical reactions as atmospheric chemists, gases, you get into the gas phase, the process is changed dramatically. So nitrate, rather than thinking of going it through NO2, I mean NO is an excellent radical scavenger, and it has a ground state of autolysis which makes NO and NO2 in the heterogeneous state, which combines with those other radicals to make nitrates and nitroso compounds. It comes back to an issue of PM, but they're very different than the ones we think about in the gas phase. So what I'm saying is we're opening an incredibly complicated can of worms here the biochemists have been trying to cope with for a number of years, and understanding this process is, in terms of the biological components and how metals and oxygen and ozone interact. It's very

complicated, but, and perhaps there needs to be a very different group of people sitting here to unravel what you really need to examine. But I think the covariance to metals of things like nitrate and metals and specific classes of organic compound are very important to understand if you're going to understand what sort of effect these have on the human body.

MS. HERING: So...

MR. CROSLEY: I don't know what to write.

MR. STEVENS: The biochemistry of free radicals.

MS. HERING: This is, it sounds like it's over and beyond.

SPEAKER: It's second tier. I mean, it's...

MS. HERING: It needs to be defined.

MR. STEVENS: It sounds like a toxicologist.

MS. HERING: It needs to be defined better. It's always going to be coupled with measurement methods, but it's not really...

MR. ZIKA: I think what we can, what we can provide for them is, I think this covariance is a very important issue, and maybe we're getting that already, but the point is, does the same particle contain the necessary components. Does it contain the

peroxides? Does it contain the metals?

MS. MIDDLEBROOK: That's an interesting, that raises an interesting question, and that is, if you have a particle that has some sort of metal in it, and it can lodge somehow in the respiratory system, and that's a humid environment, you might get uptake of some of these peroxides from the gas phase while it's in the lungs. So it's not just it being associated with the particles, the peroxides, but also what might get into the lungs and react with the metals that are lodged somehow once they're there, and that I think, is a toxicology issue looking at some of that.

MR. WHITE: A lot of the metals are free radicals. They have unpaired electrons depending upon their oxidation state, and it becomes a real can of worms when you want to try to measure the total free radical content if you have unpaired electrons on metals. That really complicates the measurement a lot.

MS. HERING: This, should I just say that this is going to require cooperative work with the toxicologist?.

MR. CROSLEY: It's really a multi-task thing. You have toxicology, depending on some of the chemistry that goes on in the particle once you have these things together as covariants, and as well as develop measurement techniques so you can find out how often it exists.

MR. ONDOV: But isn't this sort of, I mean, to measure, to get ideas of covariance and stuff, I think that's good, but we have no idea for sure whether metals have that toxicological effect in the real environment. So to go and look at the oxidation states and how they might react with everything under the sun is a bit premature.

MR. ZIKA: Well, look, but you do know, you do know that some of these metals are toxic. I mean there's microorganisms in one oxidation state that are partly toxic.

MR. ONDOV: They're toxic, yeah, but are they the main toxic components, are they, a little bit of toxic stuff is good for you, right? I mean, a tiny bit.

MS. HERING: I think, if I'm to extract this, you know, we're talking about measurements that are difficult to do, or not yet, in many cases, not yet known how to do, and there's such a host of them that to guide this, there needs to be toxicological input and some cooperative work here. Is that a, is that a fair statement?

SPEAKER: We need to get them to, the toxicologists and the health people to state what hypothesis they think we need to be testing so we can go after the right measurement techniques.

MS. HERING: Well, but they're

giving us some and then there's going to be, but we can say, well, we can't just do that, okay.

SPEAKER: It has to be, it has to be able to be up data based.

MR. CROSLEY: Yeah, and if it doesn't meet, it means, identified, then one could look at the research project.

MR. ABRAHAM: We were just talking about collecting samples from the environment. I mean, the huge changes that occur when the particles get into the lung means you're not going to be able to sample the environment and measure the chemistry of what goes on after these get into an aqueous when we talk about washing filters. When the particles get into the lung, they're right there in an aqueous environment. The volatiles are gone. There's oxygen and there are free radicals generated in the lung. But I think one of the most important things you can do is anticipate that the toxicologists are going to have questions they don't have right now and have samples collected that can be analyzed in the future, so have them preserved as stable as possible so that you could go in, if you want to look at the oxidation state of metals later, have them saved in a stable way so you can do that, even if you don't measure it right now.

MS. HERING: Save it, I think, I think there's no such thing. I mean...

MR. ABRAHAM: You're not going to be able to measure everything now that's going to be a question the toxicologist has next Monday.

MS. HERING: Yeah, I think the issue is, also though, there is no way, and it had to do with collecting reference materials, it's almost. There's no way to do that that doesn't disturb the particles.

MR. STEVENS: Not necessarily. I mean, after you collect them, if you can get them into a cold environment within a few days, the chemical properties are not going to change as dramatically as you think, Susanne. You'd be surprised that we've gone back and looked at the chemistry of samples that were collected fifteen years ago, and properties are surprisingly competent.

MR. ABRAHAM: But you can collect them and store them with less disturbance than the changes they'll undergo once they get into lungs. I don't think there's any question about that.

MR. ZIKA: Yeah, but aren't things like oxidation states and free radical, if maybe you collect them in a certain way that we can't envision that, so I mean it's a question of process. Another, you know, another way to think about this, and this is what I'd like to think bothers people in the health field when they think about the problem with the lungs, is that, you know, our bodies contain catalysis and peroxidase and

the whole variety of defense mechanisms to fight throughout the processes. The difference between our internal tissues in the lungs is that the lungs can be impregnated with hot spots, and so if you think about it in terms of a particular point where you have a metal that's capable of initiating high levels of fen type reactions, in other words, can accelerate OH radical formation in that environment, that particular spot is a problem, because the defense mechanisms may not be high enough to take care of that. I think that's the way you have to think about, about the dangers of inhaling the wrong particle or the wrong particles. Do they contain those metals? Do they contain the right components to initiate those processes in the localized environments where the body seem to can't tolerate them. That's what we need to identify. Are there particles out there like that?

SPEAKER: You're talking about size resolved particles?

MR. ZIKA: Probably size. Size, but also composition. I mean, you know, there's...

SPEAKER: Size resolved...

MS. HERING: I think we have, we have I think just, I don't know what, it's almost...

SPEAKER: It's 9:15.

MS. HERING: Not much, maybe ten minutes most. We haven't really talked about

measurements for biological materials, but actually one thing I think I'd like to follow up on Pete's suggestion and look at some priorities based on what we've put together here, and we talked about priorities on reference and calibration materials. The other issue that's come up a great deal is the organics and both how you characterize it and how you sample it. There are sampling issues and there's, there's characterization issues. Okay, can you remember back on the list of things that we've talked about is the other high priority issues here?

MR. McMURRY: I would think real time measurements.

MS. HERING: Real time measurements.

SPEAKER: What you really mean is in situ.

SPEAKER: Not necessarily. Preferably.

SPEAKER: Real time meaning ten minutes, some reality of time.

SPEAKER: 24 hours is real time, not fake time. You could just be short term.

MS. HERING: Real time measurements, if I, and then if I, the issue Peter raised I think was, actually relates to measurements that tell you what is in the air, as coming close to in situ. Do

you see what I'm saying? I'm not wording this correctly. Maybe I'm just too tired, but instead of comparing things against just what's collected on a filter, trying to do measurements in a way that tells you the most about what's, what particles are like in the air. In situ.

SPEAKER: What do you mean, in situ or the possibilities to avoid artifacts that are immune to certain substances?

MR. CROSLEY: In a respect, you really mean non-filter methods then?

MS. HERING: I just wanted to say that...

MR. McMURRY: Well, there are a number of things that are coupled here, and this is coupled with the FRM artifact question which has come up repeatedly, and it's coupled with the question of semi-volatiles which influence both inorganic and organic sampling. Somehow or other all of that ought to be tied together I think maybe into one bullet here.

MS. HERING: Yeah, that's, I'm trying to get some wording for this here on this bullet, and that's what I'm having trouble with.

MR. STEVENS: Artifact quantification is what we're trying to ask. How much nitrate evaporates? How much semi-volatiles? What particle interactions occur on the filters that change

the properties of the particle such as we can't characterize it any longer. Those types of factors, I think artifacts covers it all, but not just artifacts, under quantifying these artifacts if possible to see if we've disturbed the properties of the particles we're looking at. At least having that information, and it may give us a better insight as to what may be important.

MS. HERING: Although ultimately we'd like to get rid of them. Isn't that...

SPEAKER: But you'll never get rid of them.

SPEAKER: Because we have to be able to understand how big they are in order to get these factors.

SPEAKER: I mean, you can try, you can minimize it. I mean, you change temperature, you change pressure.

SPEAKER: Under real time, you don't mean real time examples.

MS. HERING: Real time, high time resolution, semi-continuous, continuous.

MR. SOLOMON: If it's going to be done...

MS. HERING: Automated.

MR. SOLOMON: Like more continuous, like I said it could be done with like half hour resolution on a rotating drum, for example. That's

not real time, but it's semi-continuous. So I mean, I'm just wondering if real time limits it or...

MS. HERING: Real time, I'll just say less than, less than thirty minute time resolution or less than one hour.

MR. ONDOV: If you say that's, that's the temporal resolution, but the idea is that, I mean, there's a line between real time and you can go out there and look at the dial and see 30 parts per billion, whatever it is, ozone or something like that versus getting the temporal resolution by getting the data the next day, or the next week, or the next month.

MR. STEVENS: And you also got to remember that you're making a measurement of the spot, so it's only what happens at that one spot that you took the sample, so everything got spacious, so you know, it gets to be very complicated, and I really don't know what a measurement at one location means in relationship to the whole area. We have a limited number of resources, so make a reality check here a little bit if we can.

MS. HERING: That's, that, is that a measurement issue? Well...

MR. STEVENS: Of course it's a measurement issue.

SPEAKER: It's representative. I think that was mentioned early on.

MR. NEWMAN: There's no such thing as representative. There's such a thing as completeness, and you can never be complete. You get a fraction.

MR. ZIKA: I was just, yesterday the health people were talking about what they would like to know, and they broke it down into different categories, so if you're looking at diseases that are chronic diseases, what they would like to see is a two week average over long periods of time. So it's two week sampling intervals.

MS. HERING: Interval sampling.

MR. ZIKA: Integrated samples over a long period time at a spot. Find out what one person experienced over a long period of time during their life.

MR. STEVENS: The difference between acute and...

MR. ZIKA: Right, and this is what, this is the point they were making. More as for chronic studies they wanted to see these long time interval integrated averages, but for acute studies, they would like to see...

MR. STEVENS: Short term ones.

MS. HERING: Short term ones.

MR. ZIKA: Well, hour, but maybe they said maybe we would only use that eight hour average anyways, but just out of curiosity, I'd like to

know what an hour looked like.

MS. HERING: So the time resolution we had not guessed on the long time resolution for, and I don't know that that's the recommendation that comes out of this group, but...

MR. CHING: When you dealt with real time, you really need to deal with a higher time resolved measurements, and what that helps you do is to get you down to as short a time period as possible where you can always integrate up to what people need to look at relationships between one day sampling versus every six day sampling and so forth, but if you've got the basic high resolved, high temporally resolved data, you can reconstruct.

SPEAKER: If there are no gaps.

MR. CHING: Right, continuous.

MR. CROSLEY: In the time resolution thing, this is, I was in exposure assessment yesterday, and the first response to a question I had, out of ignorance was, if you have, say one unit of something and you breathe it in for a hundred minutes, okay. Is that different from a health standpoint than not having a hundred times that level spiked for one minute, and in other words, the health effects are a non-linear kind of thing, and if you add such slow time resolution, you could miss a spike like that down in the noise, and that actually could be a very important

health consideration. Now it sounds like health folks aren't thinking along those lines.

MR. NEWMAN: Yes, they did. I worked in that exposure, they do. They want to have a table that could be very trusting compared to the table that comes out here in terms of what they would like out of the measurements.

MS. HERING: Yeah. I think that, I mean, I think it's very interesting that...

MR. NEWMAN: They definitely discussed giving very short time measurements as well, but they've also discussed, based on what they finished up this morning is, they also discussed what actually the technology can provide that group, you know, that they have to be comfortable with.

MS. HERING: Well, I think, I think that, I mean I hate to sort of put down long term sampling here as a project because we haven't really discussed here in this group, and we're not providing the motivation for it, but we could certainly include comparisons of two week sampling or, in the methods comparisons to see how valid a two week sampler is. I mean, the expensive part of doing that is doing the shorter term sampling to compare with, to compare it with.

MR. CROSLEY: If you have fast, as I pointed out, if you have a fast technique...

MS. HERING: That doesn't matter.

MR. CROSLEY: You can always bend it into one hour or two week periods. Whatever you want to do.

MS. HERING: I think it's, I think it's an issue, issue of cost.

MR. CROSLEY: So we have it available.

MS. HERING: It's an issue of, in terms of building for the future, in methods for the future, what is going to be cost effective to run and what's going to be simple to run. So there's...

MR. STEVENS: Do you mean, I mean, you're almost out, you're almost out of time here. I noticed you have organics, but are you, is this group not interested in the inorganic component of this sample?

MS. HERING: Oh, this is, no, the group definitely is, that's there. These are things that we felt should be, you know, they're priorities in terms of emphasis, things we wish to highlight.

SPEAKER: Has anybody mentioned anything about the importance of scanning electron microscopy, collecting samples compatible to scanning electron microscopy?

MS. HERING: We have mentioned it.

SPEAKER: Something early on that

you mentioned, way back in the beginning, was establishing a platform for evaluating and comparing emerging technologies.

MS. HERING: Yes.

SPEAKER: That's pretty well established now that the automation is emerging. It makes it very practical.

MR. STEVENS: The problem is that the, that the normal samples that are collected are not ideally suited. The perfect sampler, the perfect sample for scanning electron microscopy is the coarse fraction from a dichotomous sample. The reason is the coarse fraction contains only two percent, only a few percent of the fines.

MS. HERING: The fines.

MR. STEVENS: But enough so that they don't over burden the filter and secondly, you can also get the biologicals at the same time that you get the fines and that's something that's, I noticed in a couple of the groups they're talking about the biologicals, but there's no convenient way to get that except for the separate sampler, and a virtual impactor is the perfect sampler for that application. As Peter said, it ought to be the reference method. Did you say that? That's what Peter said.

MS. HERING: Okay, it's a, yeah, I think I would also put forth though that that, the

analysis of the samples for scanning microscopy, by electron microscopy needs to be introduced into, and the reasons for doing so need to be introduced into the overall measurement plans. It's not sufficient to just say, we'll collect samples so somebody can then do microscopy on them.

MR. STEVENS: I think in the criteria document they discuss some of those issues. One of the issues, of course, is differentiating sources. The second thing is the work going on on the lung tissue examinations, the length between the ambient samples and the lung tissue examinations is also part of that equation.

MS. HERING: Where's my overall slide? That falls into, that's a kind of a general, a general issue, and there is some, I mean I could list here, samples for later analysis could be useful. We've talked about that a couple of times.

MR. ABRAHAM: You know, I mean, what I was going to say is that should be listed under priorities.

MS. HERING: You want it under priorities, okay. Reference calibration.

MR. ABRAHAM: We should agree on these as a whole, right?

MR. STEVENS: Maybe it shouldn't be, I don't know.

MR. ABRAHAM: Then it should be considered for that.

MS. HERING: I wanted to highlight things that, I mean, the priorities list can't be everything, so maybe we should, should we vote or..

MR. CROSLEY: I was going to say, I want to return to the business of evaluating emerging technologies and comparing them because we want to make clear that this is a perfect place to do that. We don't want to wait until something's fully developed before we allow it to appear in the supersite. I mean, this is really the place to test those.

MR. McMURRY: And I saw this priority list as being a list of research frontiers, things that we need to work on. It's not clear that archiving filters for future analysis is something that needs a great deal of development. Maybe it's something that needs to be done as part of the health effects studies work, but I guess what is the purpose of this list? In my, if you look at most of the items that are given there, they're addressing holes in our ability to carry out measurements, and I think that's maybe a useful focus.

MS. HERING: Priorities, so we're looking at current gaps.

MR. ABRAHAM: Yeah, I guess what I meant by being along that list of holes is that the

current collection methods on the Teflon filters leave a gap. They make it very difficult to go back and do individual particle analysis.

MS. HERING: But there are means to do that.

MR. ABRAHAM: Oh, sure.

MS. HERING: I mean, we do know how to do that.

SPEAKER: Susanne, you need to finish up.

MS. HERING: So in that sense, I guess spatial variability of research.

MR. McMURRY: You know, with respect to this issue of representativeness and spatial variability, keep in mind that that's very closely tied to real time measurements because if you can do real time measurements, you can put them on the airplane and find out how representative your sample really is.

SPEAKER: It seems very sensible to include automation.

MS. HERING: That's this, implicit, and I say less than one hour with immediate results, how else are you going to do that?

SPEAKER: I agree.

MS. HERING: Automation, I'll put it in. Great.

SPEAKER: At risk of replaying an

old record, I'd like to suggest once more that one of the gaps we need to deal with somewhere along the way for prioritizing this thing is establishing data quality objectives.

MS. HERING: That's on the list as, that's not a knowledge gap, but it's something, it's on this list of overall issues, data quality, okay. I want to thank all of you for your inputs. We got through most of everything, and it's a rather large chart.

(**WHEREUPON,** the Breakout Group Session was concluded.)

C A P T I O N

The Breakout Group Session in the matter, on the date, and at the time and place set out on the title page hereof.

It was requested that the Breakout be taken by the reporter and that same be reduced to typewritten form.